Aryl Ether Cleavage by Group 9 and 10 Transition Metals: Stoichiometric Studies of Selectivity and Mechanism

Guy A. Edouard, Paul Kelley, David E. Herbert, Theodor Agapie

Division of Chemistry and Chemical Engineering, California Institute of Technology, 1200 East California Boulevard MC 127-72, Pasadena, CA 91125, United States

Supporting Information

I. Experimental Details S3
General considerations S3
Synthesis of [1,3-bis(2'-diisopropylphosphinophenyl)-5-tert-butyl-2-methoxybenzene]palladium(0) (5a). S4
Synthesis of [2,6-bis(2'-diisopropylphosphinophenyl)-4-tert-butyl-phenoxide]palladium(II)methyl (6a). S4
Synthesis of [1,3-bis(2'-diisopropylphosphinophenyl)-5-tert-butyl-2-methoxybenzene]platinum(0) (7a) S4
Synthesis of [2,6-bis(2'-diisopropylphosphinophenyl)-4-tert-butyl-phenoxide]platinum(II)methyl (8a). S4
Synthesis of 5-(tert-butyl)-1,3-diiodo-2-(4-nitrophenoxy)benzene. S5
Synthesis of 1,3-bis(2'-bromophenyl)-2-(4'-nitrophenoxy)-5-tert-butyl-benzene. S5
Synthesis of 1,3-bis(2'-bromophenyl)-2-(4'-aminophenoxy)-5-tert-butyl-benzene. S5
Synthesis of 1,3-bis(2'-bromophenyl)-2-(4'-dimethylaminophenoxy)-5-tert-butyl-benzene. S6
Synthesis of 1,3-bis(2'-diisopropylphosphinophenyl)-5-tert-butyl-2-(4'-dimethylaminophenoxy)benzene (1c). S6
Synthesis of 1,3-bis(2'-bromophenyl)-2-phenoxy-5-tert-butyl-benzene. S6
Synthesis of 1,3-bis(2'-diisopropylphosphinophenyl)-5-tert-butyl-2-phenoxy-benzene (1d). S6
Synthesis of [1,3-bis(2'-diisopropylphosphinophenyl)-5-tert-butyl-2-phenoxy-benzene]palladium(0) (10d). S7
Synthesis of [1,3-bis(2'-diisopropylphosphinophenyl)-5-tert-butyl-2-phenoxy-benzene]platinum(0) (11d). S7
Synthesis of [1,3-bis(2'-diisopropylphosphinophenyl)-5-tert-butyl-phenyl]nickel(II) (4'-dimethylaminophenoxide) (12c). S7
Synthesis of [1,3-bis(2'-diisopropylphosphinophenyl)-5-tert-butyl-phenyl]palladium(II)phenoxide (13d). S7
Synthesis of [1,3-bis(2'-diisopropylphosphinophenyl)-5-tert-butyl-phenyl]platinum(II)phenoxide (14d) S8
Synthesis of [1,3-bis(2'-diisopropylphosphinophenyl)-5-tert-butyl-2-methoxybenzene]rhodium(I) (1,5-cyclooctadiene)chloride (15a). S8
Synthesis of [1,3-bis(2'-diisopropylphosphinophenyl)-5-tert-butyl-benzene]rhodium(I)chloride (19a). S8
Synthesis of 1,3-bis(2'bromophenyl)-5-tert-butyl-benzene. S9
Synthesis of 1,3-bis(2'-diisopropylphosphinophenyl)-5-tert-butyl-benzene (1e). S9
Synthesis of [1,3-bis(2'-diisopropylphosphinophenyl)-5-tert-butyl-2-methoxybenzene]rhodium(I) (carbonyl)chloride (23a). S9
Synthesis of [2,6-bis(2'-diisopropylphosphinophenyl)-4-tert-butyl-phenoxide]rhodium(I)carbonyl (24a). S9
Synthesis of 5-(tert-butyl)-1,3-diiodo-2-(methoxymethoxy)benzene. S10
Synthesis of 1,3-bis(2'-bromophenyl)-5-tert-butyl-2-(methoxymethoxy)benzene. S11
Synthesis of 2,6-bis(2'-diisopropylphosphinophenyl)-4-tert-butyl-phenol (1f). S11
Synthesis of [1,3-bis(2'-diisopropylphosphinophenyl)-5-tert-butyl-benzene]rhodium(I)(carbonyl)chloride (26a). S11
Synthesis of [1,3-bis(2'-diisopropylphosphinophenyl)-5-tert-butyl-2-methoxybenzene]iridium(I) (1,5-cyclooctadiene)chloride (27a). S12
Synthesis of [2,6-bis(2'-diisopropylphosphinophenyl)-4-tert-butyl-phenoxide]iridium(I)carbonyl (28a). S13
Synthesis of [1,3-bis(2'-diisopropylphosphinophenyl)-5-tert-butyl-2-methoxybenzene]iridium(I) (carbonyl)chloride (29a). S14
Synthesis of [2,6-bis(2'-diisopropylphosphinophenyl)-4-tert-butyl-phenoxide]nickel(II)chloride (32a). S14
Synthesis of [2,6-bis(2'-diisopropylphosphinophenyl)-4-dimethylamino-phenoxide]nickel(II)chloride (32b). S15
Synthesis of [1,3-bis(2'-diisopropylphosphinophenyl)-5-tert-butyl-2-methoxybenzene]palladium(II) chloride (33a). S15
Synthesis of [(1,3-bis(2'-diisopropylphosphinophenyl)-5-tert-butyl-2-methoxybenzene)palladium(II) bisacetontrile][tetrafluoroborate] (34a). S15
Synthesis of [2,6-bis(2'-diisopropylphosphinophenyl)-4-tert-butyl-phenoxide]palladium(II)chloride (35a). S15
Synthesis of [1,3-bis(2'-diisopropylphosphinophenyl)-5-tert-butyl-2-methoxybenzene]platinum(II) chloride (36a). S16
Synthesis of [2,6-bis(2'-diisopropylphosphinophenyl)-4-tert-butyl-phenoxide]platinum(II)chloride (37a). S16
Synthesis of [1,3-bis(2'-diisopropylphosphinophenyl)-5-tert-butyl-2-methoxybenzene]cobalt(I)bromide (38a). S16

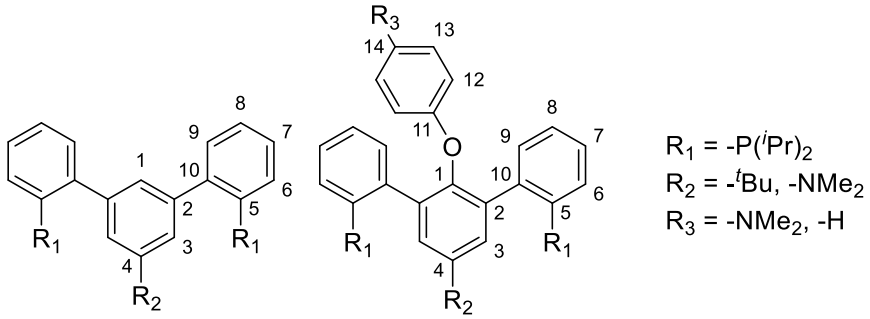
II. Crystallographic Data S17
Table S1. Crystal and refinement data for 5a, 8a, 19a, 26a. S17
Table S2. Crystal and refinement data for 28a, 32b, 34a, 38a. S17

III. Nuclear Magnetic Resonance Spectra S18
Figure S1. ^{1}H NMR spectrum of 5a in C_6D_6. S18
Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of 5a in C_6D_6. S18
Figure S3. $^{31}P\{^{1}H\}$ NMR spectrum of 5a in C_6D_6. S18
Figure S4. ^{1}H NMR spectrum of 6a in C_6D_6. S19
Figure S5. $^{13}C\{^{1}H\}$ NMR spectrum of 6a in C_6D_6. S19
Figure S6. $^{31}P\{^{1}H\}$ NMR spectrum of 6a in C_6D_6. S19
Figure S7. ^{1}H NMR spectrum of 7a in C_6D_6. S20
Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum of 7a in C_6D_6. S20
Figure S9. $^{31}P\{^{1}H\}$ NMR spectrum of 7a in C_6D_6. S20
Figure S10. ^{1}H NMR spectrum of 8a in C_6D_6. S21
Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum of 8a in C_6D_6. S21
Figure S12. $^{31}P\{^{1}H\}$ NMR spectrum of 8a in C_6D_6. S21
Figure S13. ^{1}H NMR spectrum of 5-(tert-butyl)-1,3-diiodo-2-(4-nitrophenoxy)benzene in $CDCl_3$. S22
Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum of 5-(tert-butyl)-1,3-diiodo-2-(4-nitrophenoxy)benzene in $CDCl_3$. S22
Figure S15. ^{1}H NMR spectrum of 1,3-bis(2'-bromophenyl)-2-(4'-nitrophenoxy)-5-tert-butyl-benzene in $CDCl_3$ S22
Figure S16. ^{1}H NMR spectrum of 1,3-bis(2'-bromophenyl)-2-(4'-aminophenoxy)-5-tert-butyl-benzene in $CDCl_3$. S23
Figure S17. ^{1}H NMR spectrum of 1,3-bis(2'-bromophenyl)-2-(4'-dimethylaminophenoxy)-5-tert-butyl-benzene in C_6D_6. S23
Figure S18. ^{1}H NMR spectrum of 1c at 25 °C in C_6D_6. S23
Figure S19. $^{13}C\{^{1}H\}$ NMR spectrum of 1c at 25 °C in C_6D_6. S24
Figure S20. $^{31}P\{^{1}H\}$ NMR spectrum of 1c at 25 °C in C_6D_6. S24
Figure S21. ^{1}H NMR spectrum of 1c at 70 °C in C_6D_6. S24
Figure S22. ^{1}H NMR spectrum of 1,3-bis(2'-bromophenyl)-2-phenoxy-5-tert-butyl-benzene in $CDCl_3$. S25
Figure S23. $^{13}C\{^{1}H\}$ NMR spectrum of 1,3-bis(2'-bromophenyl)-2-phenoxy-5-tert-butyl-benzene in $CDCl_3$. S25
Figure S24. ^{1}H NMR spectrum of 1d at 25 °C in $CDCl_3$. S25
Figure S25. ^{1}H NMR spectrum of 1d at 25 °C in C_6D_6. S26
Figure S26. $^{13}C\{^{1}H\}$ NMR of 1d at 25 °C in $CDCl_3$. S26
Figure S27. $^{31}P\{^{1}H\}$ NMR of 1d at 25 °C in $CDCl_3$. S26
Figure S28. $^{31}P\{^{1}H\}$ NMR of 1d at 25 °C in C_6D_6. S27
Figure S29. ^{1}H NMR spectrum of 1d at 70 °C in C_6D_6. S27
Figure S30. $^{13}C\{^{1}H\}$ NMR spectrum of 1d at 70 °C in C_6D_6. S27
Figure S31. $^{31}P\{^{1}H\}$ NMR spectrum of 1d at 70 °C in C_6D_6. S28
Figure S32. ^{1}H NMR spectrum of 10d in C_6D_6. S28
Figure S33. $^{13}C\{^{1}H\}$ NMR spectrum of 10d in C_6D_6. S28
Figure S34. $^{31}P\{^{1}H\}$ NMR spectrum of 10d in C_6D_6. S29
Figure S35. ^{1}H NMR spectrum of 11d in C_6D_6. S29
Figure S36. $^{13}C\{^{1}H\}$ NMR spectrum of 11d in C_6D_6. S29
Figure S37. $^{31}P\{^{1}H\}$ NMR spectrum of 11d in C_6D_6. S30
Figure S38. ^{1}H NMR spectrum of 12c in C_6D_6. S30
Figure S39. $^{13}C\{^{1}H\}$ NMR spectrum of 12c in C_6D_6. S30
Figure S40. $^{31}P\{^{1}H\}$ NMR spectrum of 12c in C_6D_6. S31
Figure S41. ^{1}H NMR spectrum of 13d in C_6D_6. S31
Figure S42. $^{13}C\{^{1}H\}$ NMR spectrum of 13d in C_6D_6. S31
Figure S43. $^{31}P\{^{1}H\}$ NMR spectrum of 13d in C_6D_6. S32
Figure S44. ^{1}H NMR spectrum of 14d in C_6D_6. S32
Figure S45. $^{13}C\{^{1}H\}$ NMR spectrum of 14d in C_6D_6. S32
Figure S46. $^{31}P\{^{1}H\}$ NMR spectrum of 14d in C_6D_6. S33
Figure S47. ^{1}H NMR spectrum of 15a in C_6D_6. S33
Figure S48. $^{13}C\{^{1}H\}$ NMR spectrum of 15a in C_6D_6. S33
Figure S49. $^{31}P\{^{1}H\}$ NMR spectrum of 15a in C_6D_6. S34
Figure S50. ^{1}H NMR spectrum of 19a at 25 °C in C_6D_6. S34
Figure S51. $^{31}P\{^{1}H\}$ NMR spectrum of 19a at 25 °C in C_6D_6. S34
Figure S52. $^{13}C\{^{1}H\}$ NMR spectrum of 19a at 70 °C in C_6D_6. S35
Figure S53. $^{31}P\{^{1}H\}$ NMR spectrum of 19a at 70 °C in C_6D_6. S35
Figure S54. ^{1}H NMR of 1,3-bis(2'bromophenyl)-5-tert-butyl-benzene in $CDCl_3$. S35
Figure S55. ^{1}H NMR spectrum of 1e in C_6D_6. S36
Figure S56. $^{13}C\{^{1}H\}$ NMR spectrum of 1e in $CDCl_3$. S36
Figure S57. $^{31}P\{^{1}H\}$ NMR spectrum of 1e in C_6D_6. S36
Figure S58. ^{1}H NMR spectrum of 23a in C_6D_6. S37
Figure S59. $^{13}C\{^{1}H\}$ NMR spectrum of 23a in C_6D_6. S37
Figure S60. $^{31}P\{^{1}H\}$ NMR spectrum of 23a in C_6D_6. S37
Figure S61. ^{1}H NMR spectrum of 24a in C_6D_6. S38
Figure S62. $^{13}C\{^{1}H\}$ NMR spectrum of 24a in C_6D_6. S38
Figure S63. $^{31}P\{^{1}H\}$ NMR spectrum of 24a in C_6D_6. S38
Figure S64. ^{1}H NMR spectrum of 5-(tert-butyl)-1,3-diiodo-2-(methoxymethoxy)benzene in $CDCl_3$. S39
Figure S65. $^{13}C\{^{1}H\}$ NMR spectrum of 5-(tert-butyl)-1,3-diiodo-2-(methoxymethoxy)benzene in $CDCl_3$. S39
Figure S66. ^{1}H NMR spectrum of 1,3-bis(2'-bromophenyl)-5-tert-butyl-2-(methoxymethoxy)benzene in $CDCl_3$. S39
Figure S67. ^{1}H NMR spectrum of 1f at 25 °C in C_6D_6. S40
Figure S68. $^{31}P\{^{1}H\}$ NMR spectrum of 1f at 25 °C in C_6D_6. S40

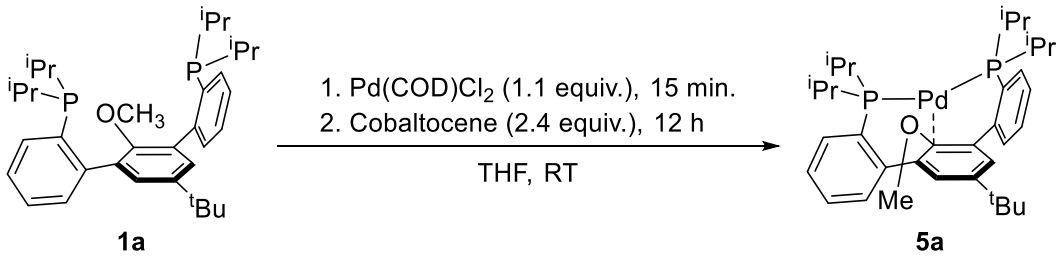
Figure S69. ^{1}H NMR spectrum of 1f at 70 °C in C_6D_6. **S40**
Figure S70. $^{13}C\{^{1}H\}$ NMR spectrum of 1f at 70 °C in C_6D_6. **S41**
Figure S71. $^{31}P\{^{1}H\}$ NMR spectrum of 1f at 70 °C in C_6D_6. **S41**
Figure S72. ^{1}H NMR spectrum of 26a in C_6D_6. **S41**
Figure S73. $^{13}C\{^{1}H\}$ NMR spectrum of 26a in C_6D_6. **S42**
Figure S74. $^{31}P\{^{1}H\}$ NMR spectrum of 26a in C_6D_6. **S42**
Figure S75. ^{1}H NMR spectrum of 27a in C_6D_6. **S42**
Figure S76. $^{13}C\{^{1}H\}$ NMR spectrum of 27a in C_6D_6. **S43**
Figure S77. $^{31}P\{^{1}H\}$ NMR spectrum of 27a in C_6D_6. **S43**
Figure S78. ^{1}H NMR spectrum of 28a in C_6D_6. **S43**
Figure S79. $^{13}C\{^{1}H\}$ NMR spectrum of 28a in C_6D_6. **S44**
Figure S80. $^{31}P\{^{1}H\}$ NMR spectrum of 28a in C_6D_6. **S44**
Figure S81. ^{1}H NMR spectrum of 29a in C_6D_6. **S44**
Figure S82. $^{13}C\{^{1}H\}$ NMR spectrum of 29a in C_6D_6. **S45**
Figure S83. $^{31}P\{^{1}H\}$ NMR spectrum of 29a in C_6D_6. **S45**
Figure S84. ^{1}H NMR spectrum of 32a in C_6D_6. **S45**
Figure S85. $^{13}C\{^{1}H\}$ NMR spectrum of 32a in C_6D_6. **S46**
Figure S86. $^{31}P\{^{1}H\}$ NMR spectrum of 32a in C_6D_6. **S46**
Figure S87. ^{1}H NMR spectrum of 32b in C_6D_6. **S46**
Figure S88. $^{13}C\{^{1}H\}$ NMR spectrum of 32b in C_6D_6. **S47**
Figure S89. $^{31}P\{^{1}H\}$ NMR spectrum of 32b in C_6D_6. **S47**
Figure S90. ^{1}H NMR spectrum of 33a in C_6D_6. **S47**
Figure S91. $^{13}C\{^{1}H\}$ NMR spectrum of 33a in C_6D_6. **S48**
Figure S92. $^{31}P\{^{1}H\}$ NMR spectrum of 33a in C_6D_6. **S48**
Figure S93. ^{1}H NMR spectrum of 34a in CD_3CN. **S48**
Figure S94. $^{13}C\{^{1}H\}$ NMR spectrum of 34a in CD_3CN. **S49**
Figure S95. ^{19}F NMR spectrum of 34a in CD_3CN. **S49**
Figure S96. $^{31}P\{^{1}H\}$ NMR spectrum of 34a in CD_3CN. **S49**
Figure S97. ^{1}H NMR spectrum of 35a in C_6D_6. **S50**
Figure S98. $^{13}C\{^{1}H\}$ NMR spectrum of 35a in C_6D_6. **S50**
Figure S99. $^{31}P\{^{1}H\}$ NMR spectrum of 35a in C_6D_6. **S50**
Figure S100. ^{1}H NMR spectrum of 36a in C_6D_6. **S51**
Figure S101. $^{13}C\{^{1}H\}$ NMR spectrum of 36a in C_6D_6. **S51**
Figure S102. $^{31}P\{^{1}H\}$ NMR spectrum of 36a in C_6D_6. **S51**
Figure S103. ^{1}H NMR spectrum of 37a in C_6D_6. **S52**
Figure S104. $^{13}C\{^{1}H\}$ NMR spectrum of 37a in C_6D_6. **S52**
Figure S105. $^{31}P\{^{1}H\}$ NMR spectrum of 37a in C_6D_6. **S52**
Figure S106. ^{1}H NMR spectrum of 38a in C_6D_6. **S53**

I. Experimental Details

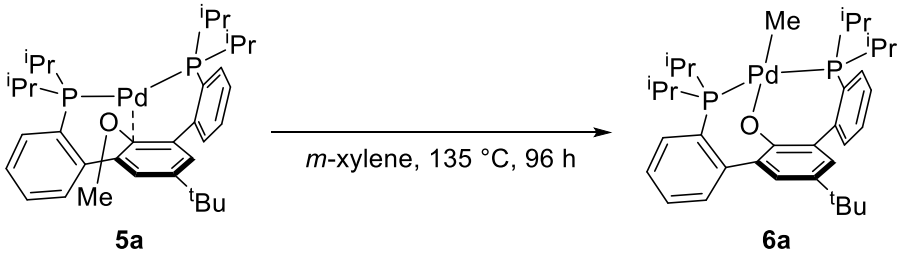
General considerations: In the following complexes, the carbons of the terphenyl backbone are assigned using the following schemes:



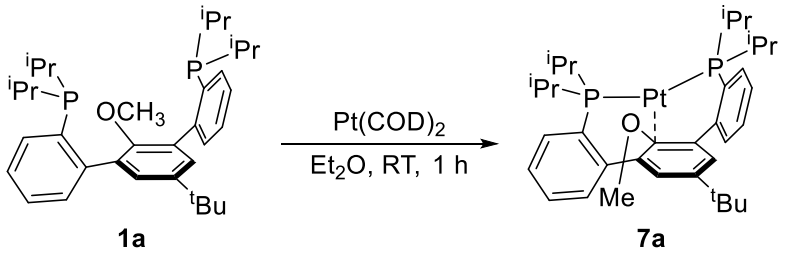
Synthesis of [1,3-bis(2'-diisopropylphosphinophenyl)-5-tert-butyl-2-methoxybenzene]palladium(0) (5a).



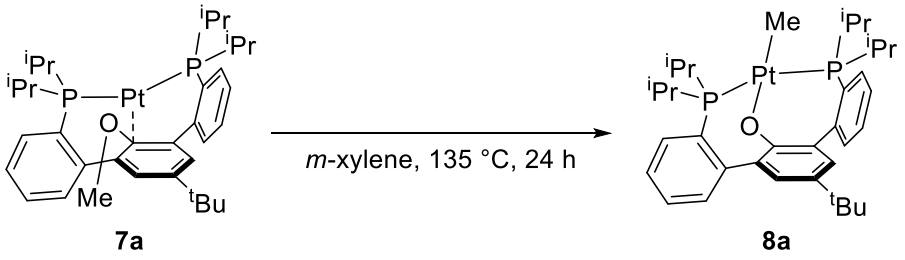
Synthesis of [2,6-bis(2'-diisopropylphosphinophenyl)-4-tert-butyl-phenoxide]palladium(II)methyl (6a).



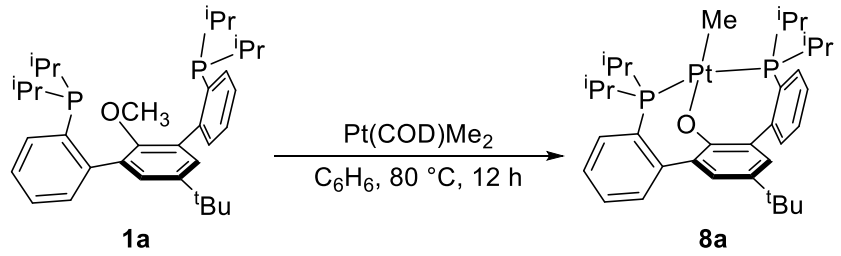
Synthesis of [1,3-bis(2'-diisopropylphosphinophenyl)-5-tert-butyl-2-methoxybenzene]platinum(0) (7a).



Synthesis of [2,6-bis(2'-diisopropylphosphinophenyl)-4-tert-butyl-phenoxide]platinum(II)methyl (8a).



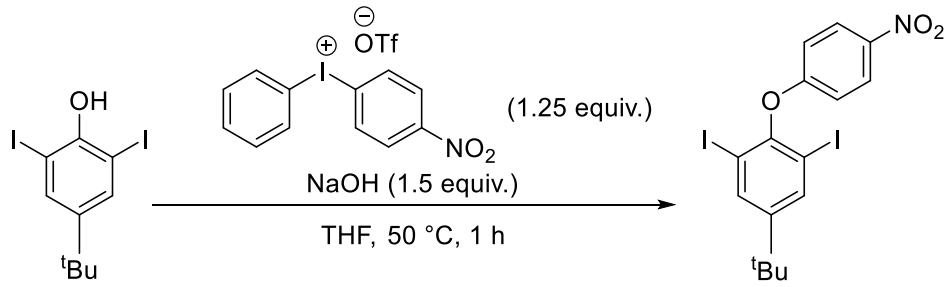
Method A



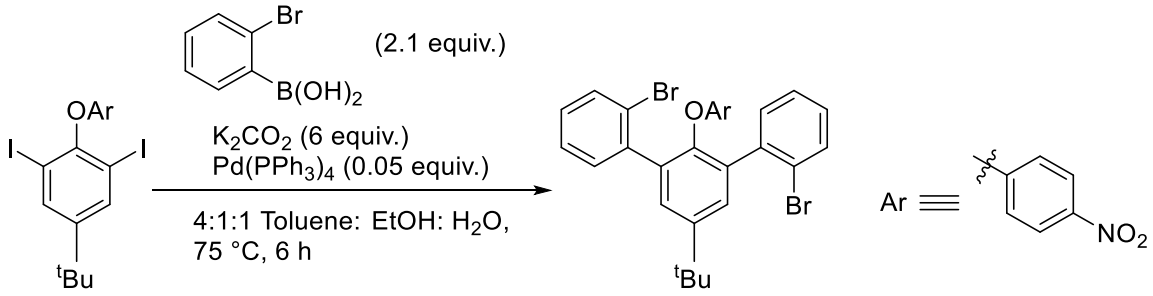
1a **8a**

Method B

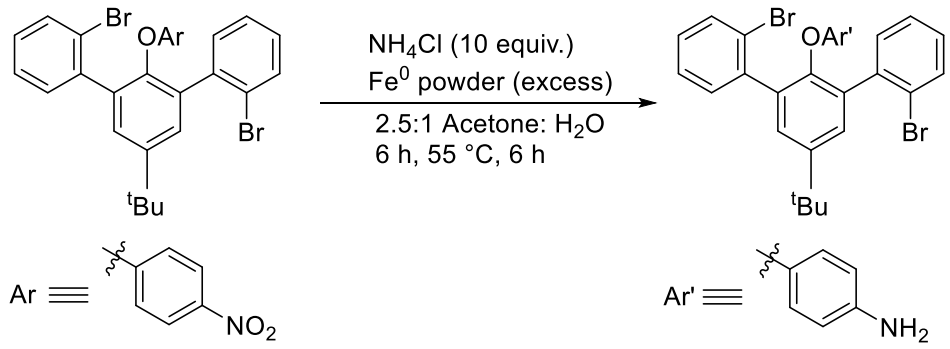
Synthesis of 5-(tert-butyl)-1,3-diiodo-2-(4-nitrophenoxy)benzene.



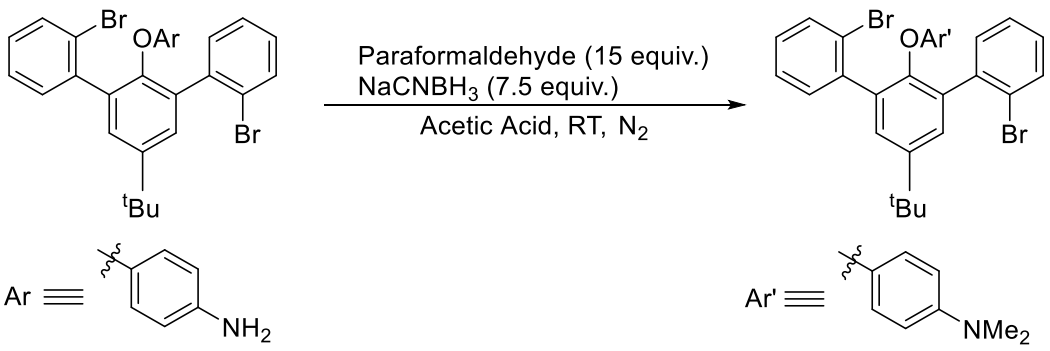
Synthesis of 1,3-bis(2'-bromophenyl)-2-(4'-nitrophenoxy)-5-tert-butyl-benzene.



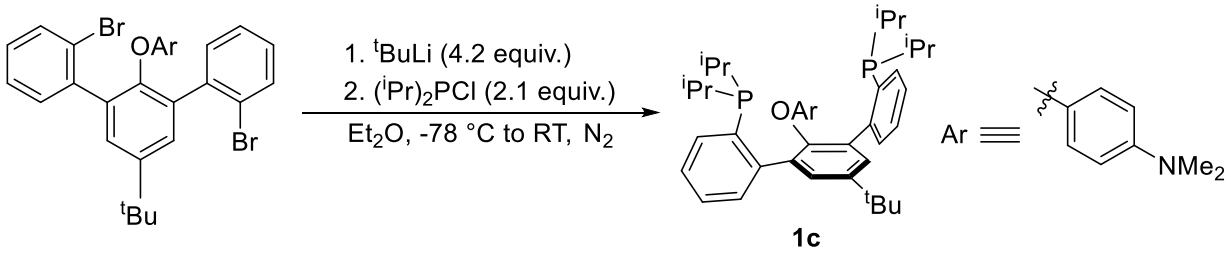
Synthesis of 1,3-bis(2'-bromophenyl)-2-(4'-aminophenoxy)-5-tert-butyl-benzene.



Synthesis of 1,3-bis(2'-bromophenyl)-2-(4'-dimethylaminophenoxy)-5-tert-butyl-benzene.

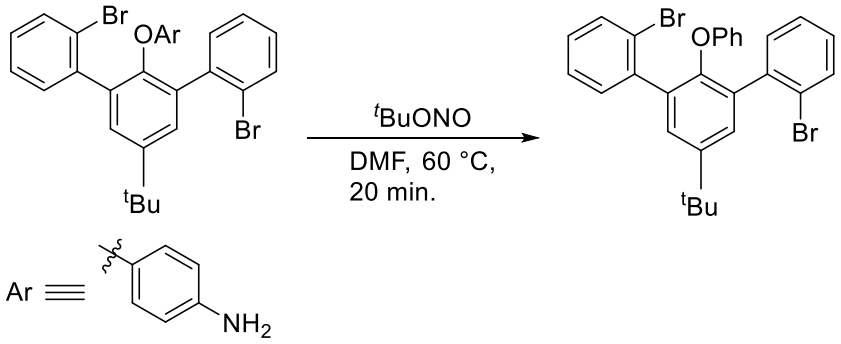


Synthesis of 1,3-bis(2'-diisopropylphosphinophenyl)-5-tert-butyl-2-(4'-dimethylaminophenoxy)benzene (1c).

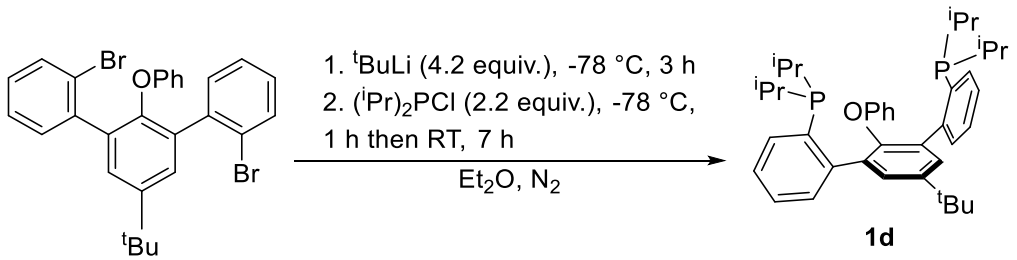


1c

Synthesis of 1,3-bis(2'-bromophenyl)-2-phenoxy-5-tert-butyl-benzene.

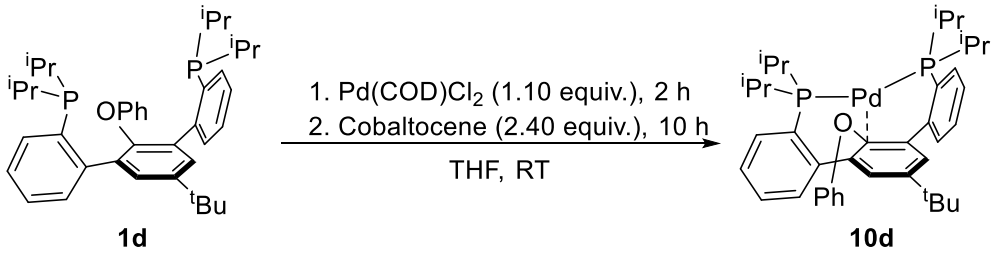


Synthesis of Synthesis of 1,3-bis(2'-diisopropylphosphinophenyl)-5-tert-butyl-2-phenoxy-benzene (1d).

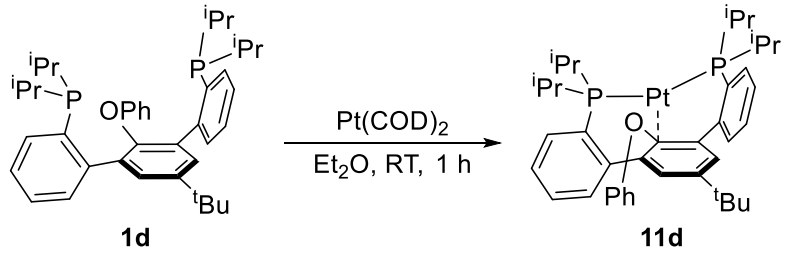


1d

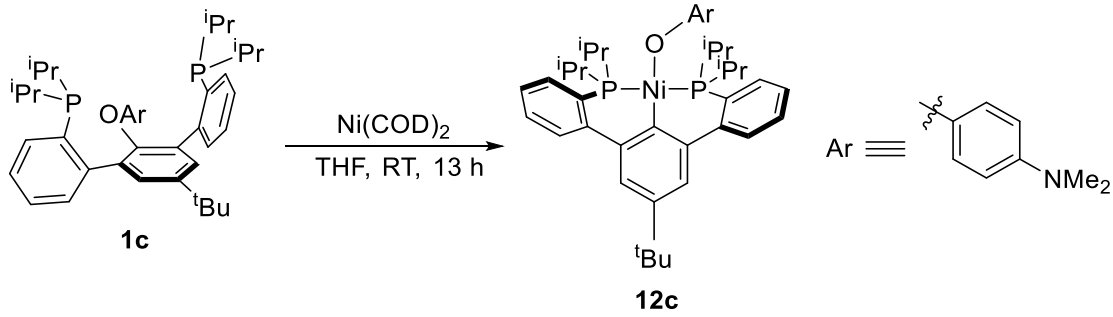
Synthesis of [1,3-bis(2'-diisopropylphosphinophenyl)-5-tert-butyl-2-phenoxy-benzene]palladium(0) (10d).



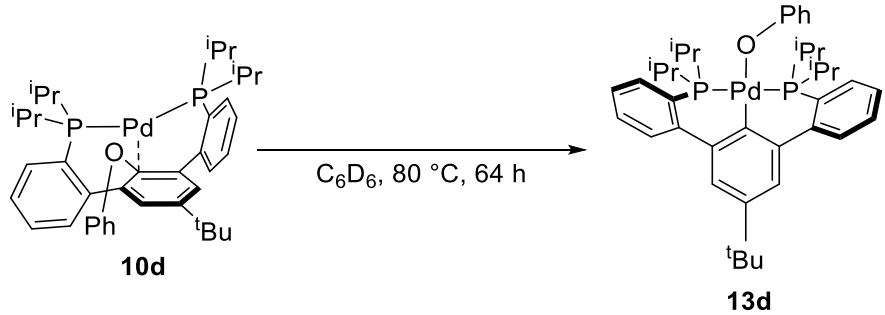
Synthesis of [1,3-bis(2'-diisopropylphosphinophenyl)-5-tert-butyl-2-phenoxy-benzene]platinum(0) (11d).



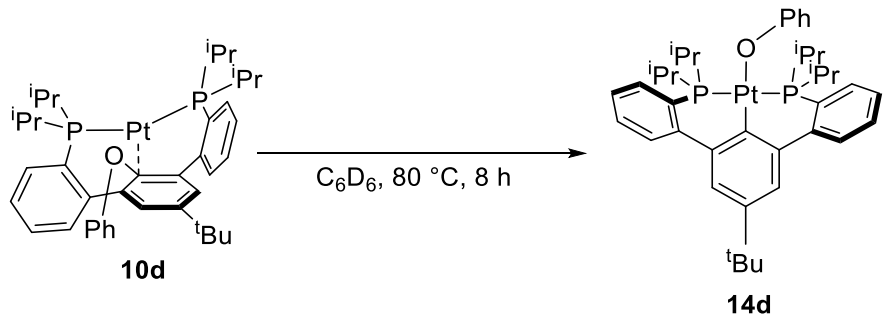
Synthesis of [1,3-bis(2'-diisopropylphosphinophenyl)-5-tert-butyl-phenyl]nickel(II)(4'-dimethylamino phenoxide) (12c).



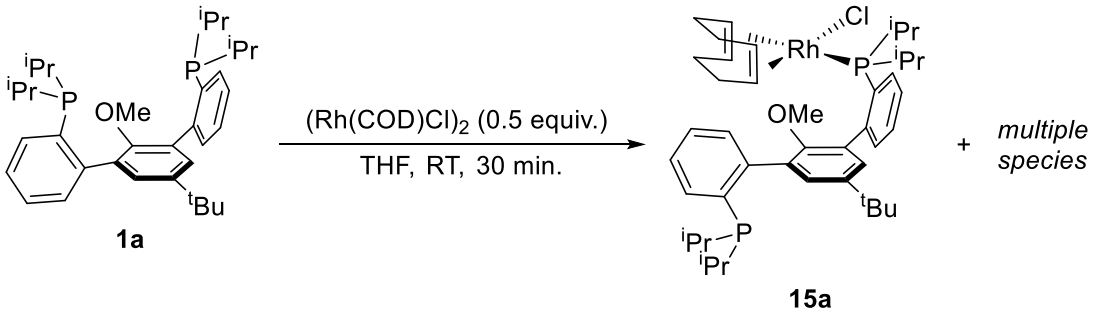
Synthesis of [1,3-bis(2'-diisopropylphosphinophenyl)-5-tert-butyl-phenyl]palladium(II)phenoxide (13d).



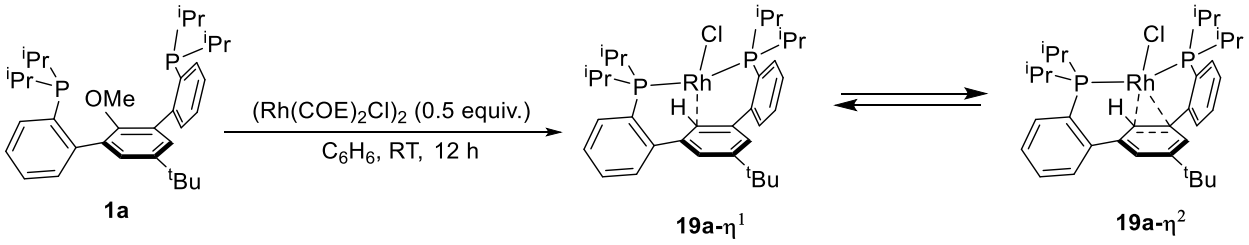
Synthesis of [1,3-bis(2'-diisopropylphosphinophenyl)-5-tert-butyl-phenyl]platinum(II)phenoxide (14d).



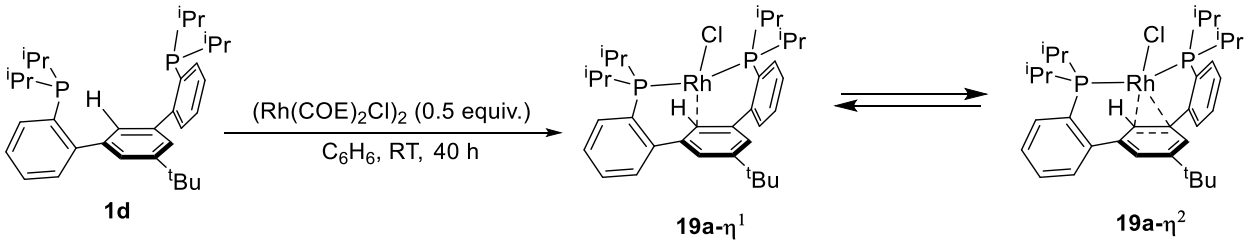
Synthesis of [1,3-bis(2'-diisopropylphosphinophenyl)-5-tert-butyl-2-methoxybenzene]rhodium(I) (1,5-cyclooctadiene)chloride (15a).



Synthesis of [1,3-bis(2'-diisopropylphosphinophenyl)-5-tert-butyl-benzene]rhodium(I)chloride (19a).

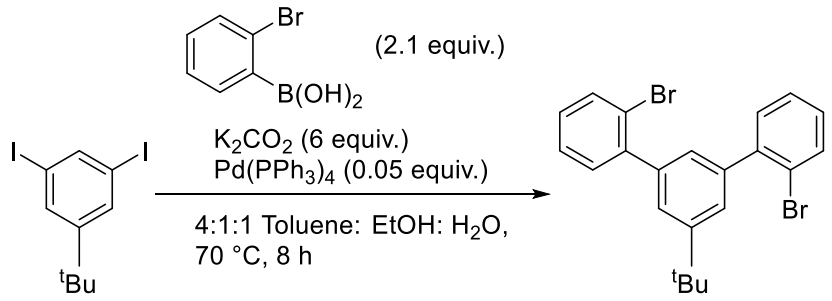


Method A

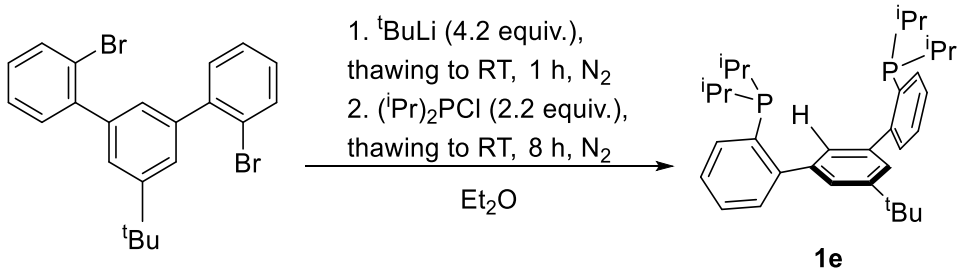


Method B

Synthesis of 1,3-bis(2'bromophenyl)-5-*tert*-butyl-benzene

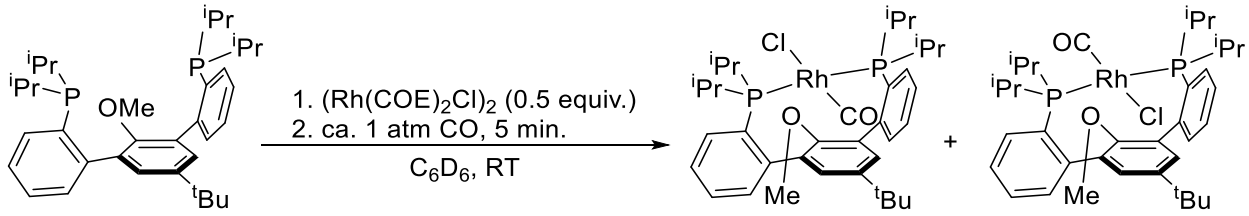


Synthesis of 1,3-bis(2'-diisopropylphosphinophenyl)-5-tert-butyl-benzene (1e)



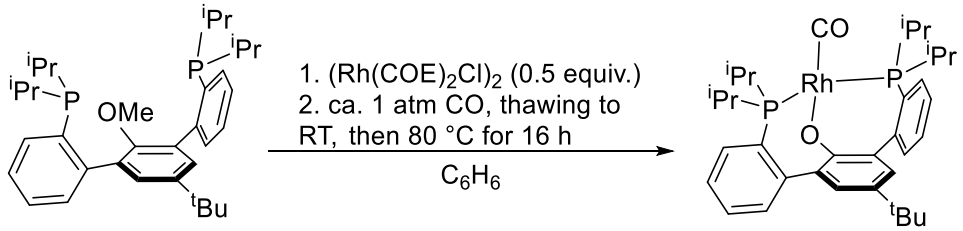
1e

Synthesis of [1,3-bis(2'-diisopropylphosphinophenyl)-5-tert-butyl-2-methoxybenzene]rhodium(I) (carbonyl)chloride (23a).



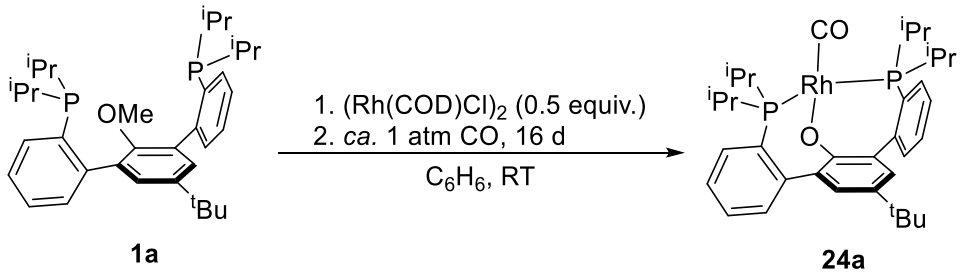
1a **23a**

Synthesis of [2,6-bis(2'-diisopropylphosphinophenyl)-4-tert-butyl-phenoxide]rhodium(I)carbonyl (24a).

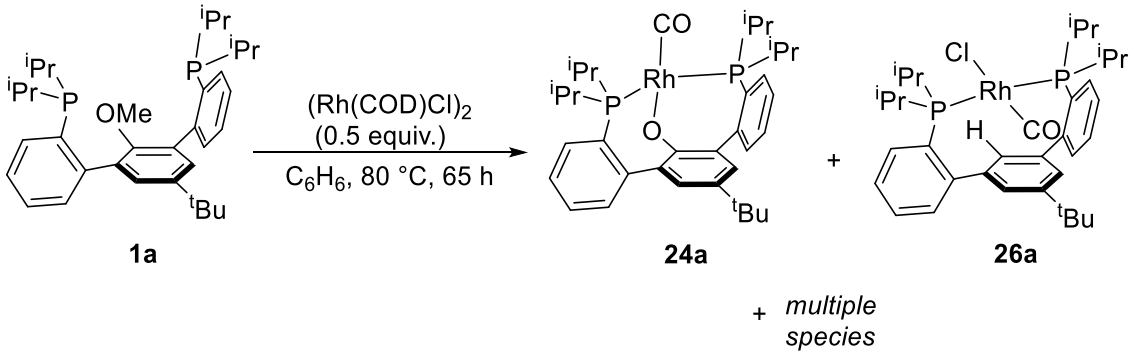


1a **24a**

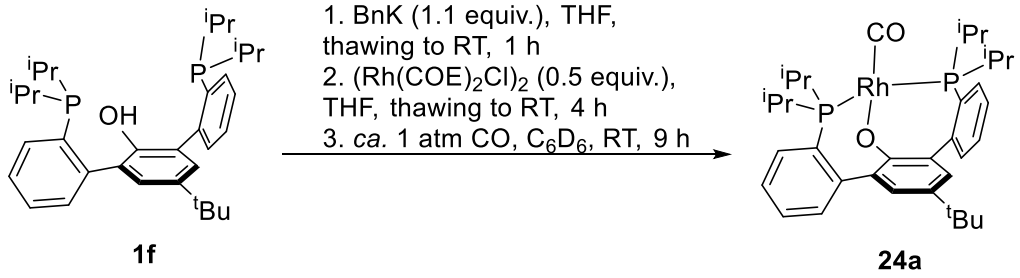
Method A



Method B

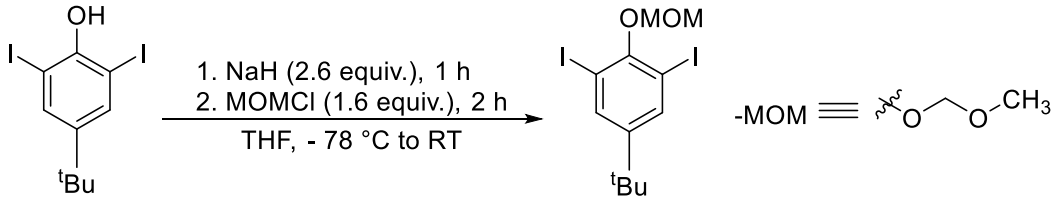


Method C



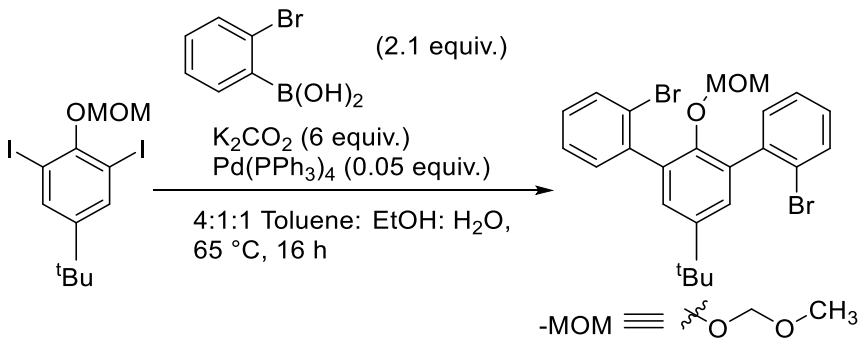
Method D

Synthesis of 5-(tert-butyl)-1,3-diiodo-2-(methoxymethoxy)benzene.

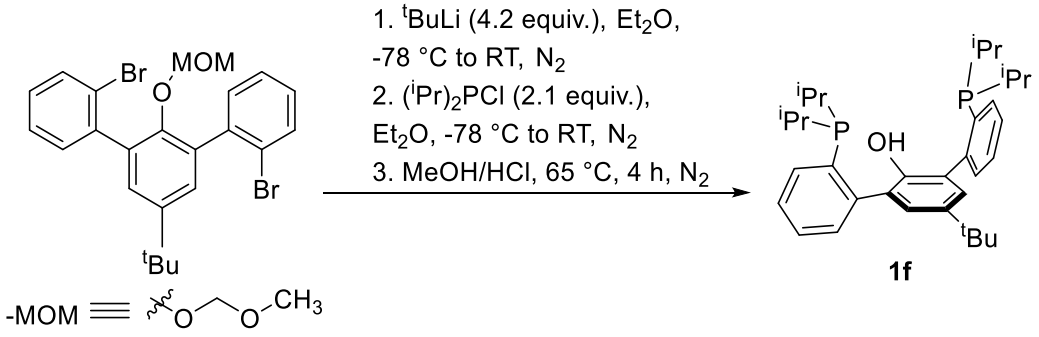


CAUTION: MOMCl is a known carcinogen.

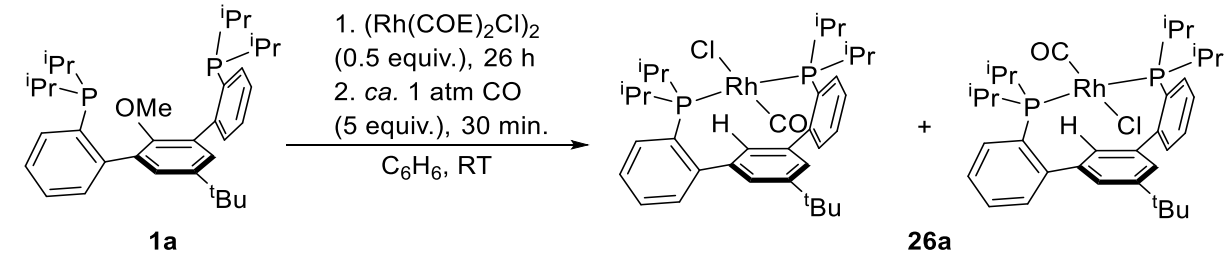
Synthesis of 1,3-bis(2'-bromophenyl)-5-tert-butyl-2-(methoxymethoxy)benzene.



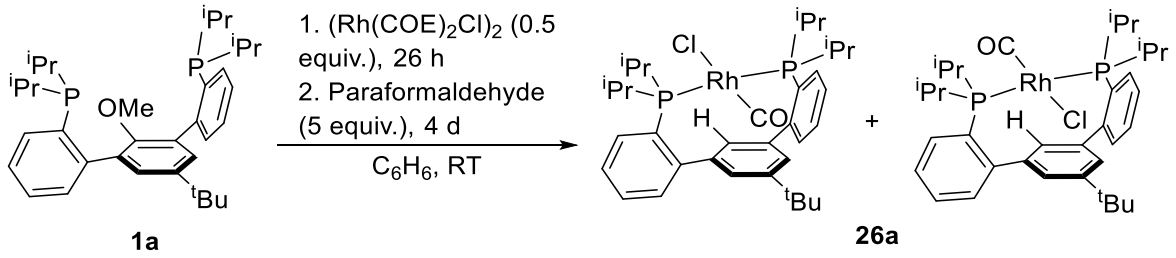
Synthesis of 2,6-bis(2'-diisopropylphosphinophenyl)-4-tert-butyl-phenol (1f).



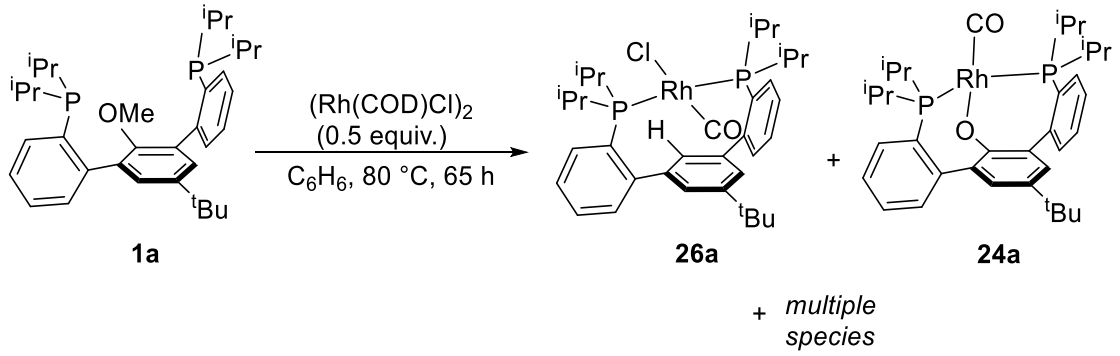
Synthesis of [1,3-bis(2'-diisopropylphosphinophenyl)-5-tert-butyl-benzene]rhodium(I)(carbonyl) chloride (26a).



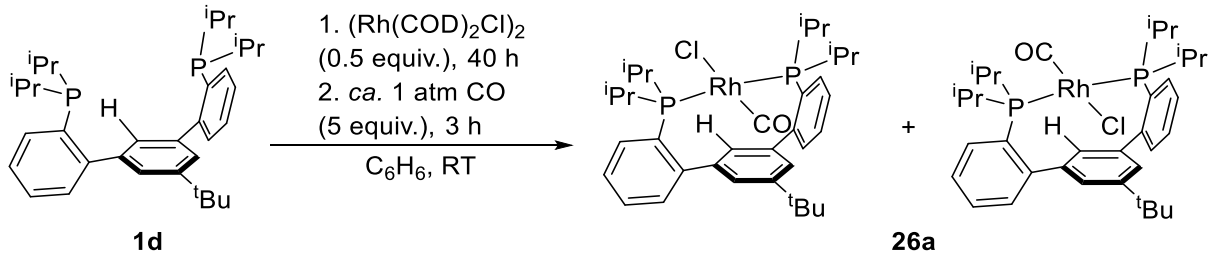
Method A



Method B

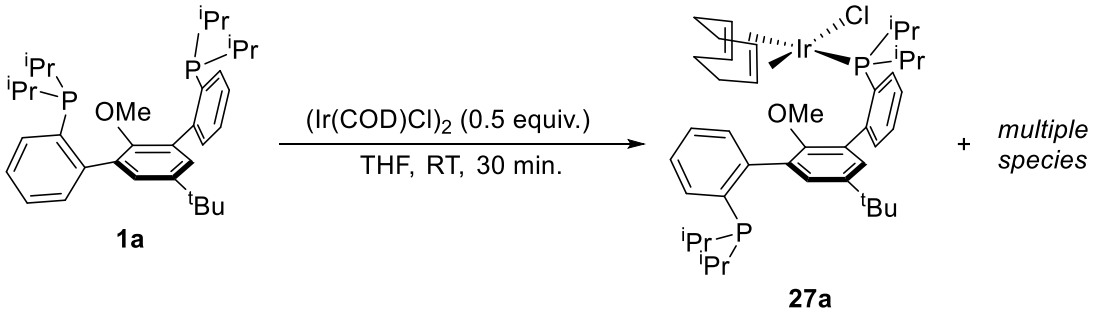


Method C

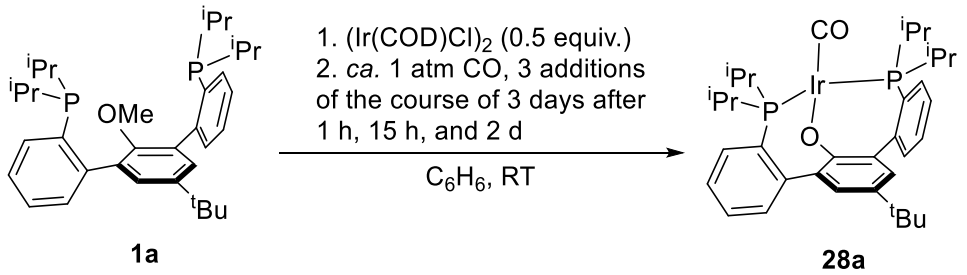


Method D

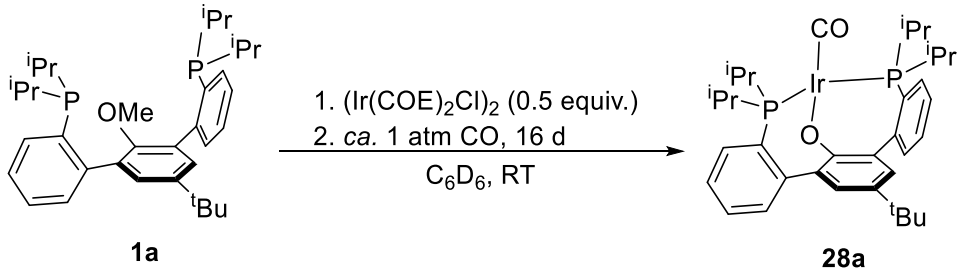
Synthesis of [1,3-bis(2'-diisopropylphosphinophenyl)-5-tert-butyl-2-methoxybenzene]iridium(I) (1,5-cyclooctadiene)chloride (27a).



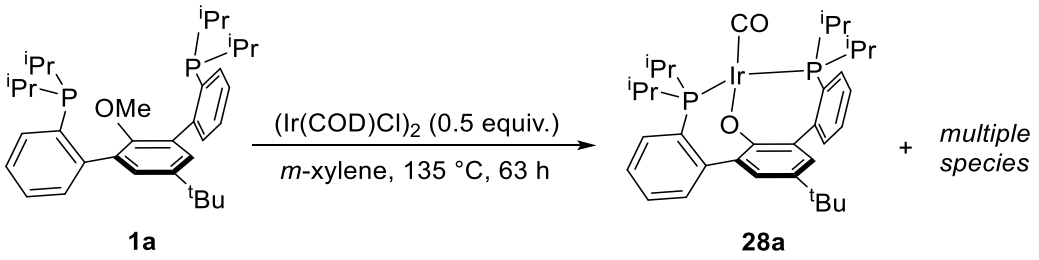
Synthesis of [2,6-bis(2'-diisopropylphosphinophenyl)-4-tert-butyl-phenoxide]iridium(I)carbonyl (28a).



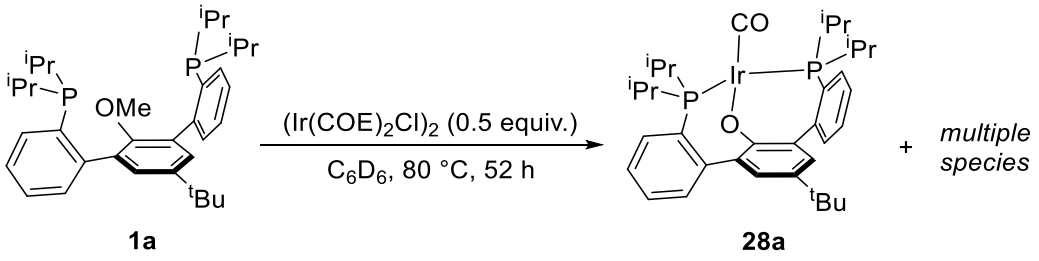
Method A



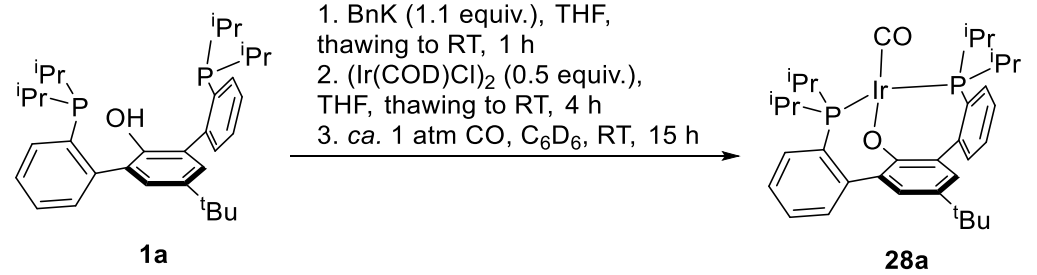
Method B



Method C

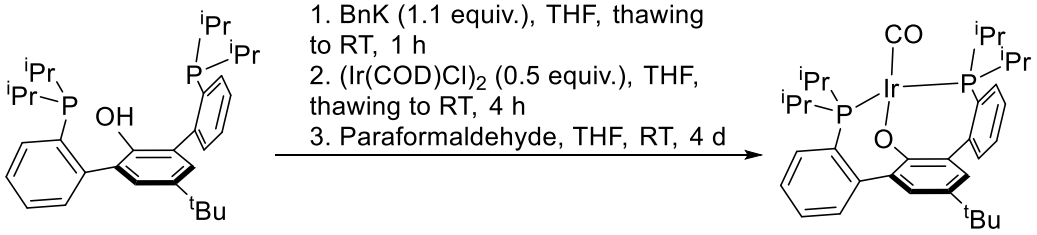


Method D



1a **28a**

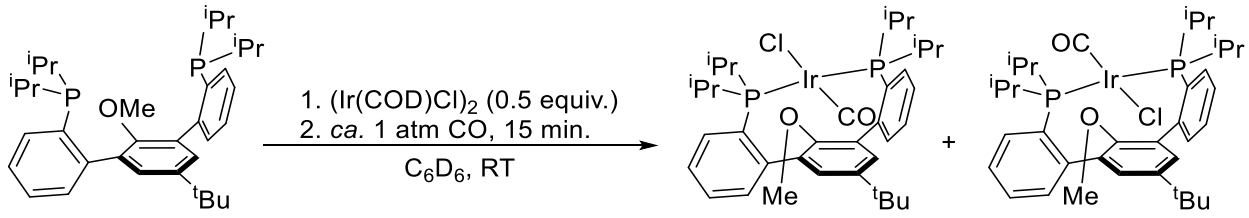
Method E



1f **28a**

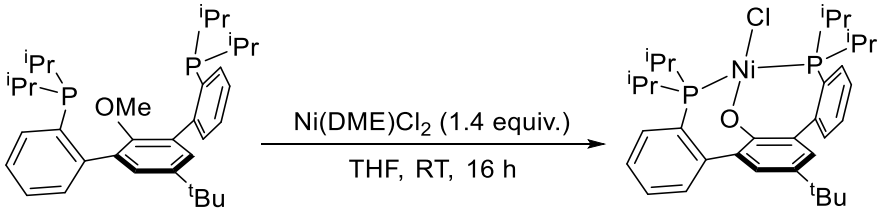
Method F

Synthesis of [1,3-bis(2'-diisopropylphosphinophenyl)-5-tert-butyl-2-methoxybenzene]iridium(I) (carbonyl)chloride (29a).



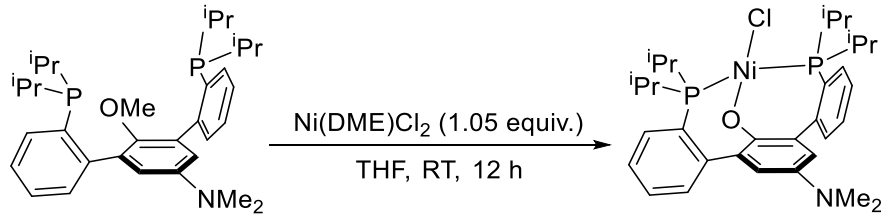
1a **29a**

Synthesis of [2,6-bis(2'-diisopropylphosphinophenyl)-4-tert-butyl-phenoxide]nickel(II)chloride (32a).



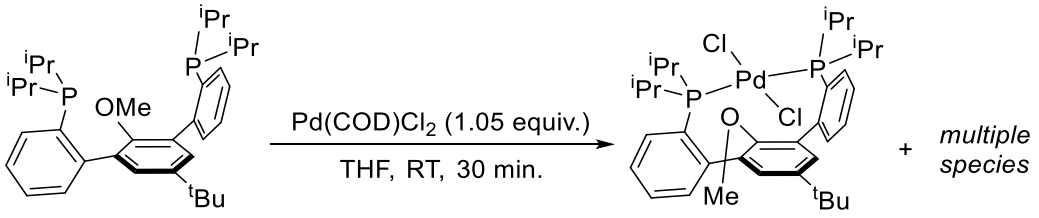
1a **32a**

Synthesis of [2,6-bis(2'-diisopropylphosphinophenyl)-4-dimethylamino-phenoxide] nickel(II)chloride (32b).



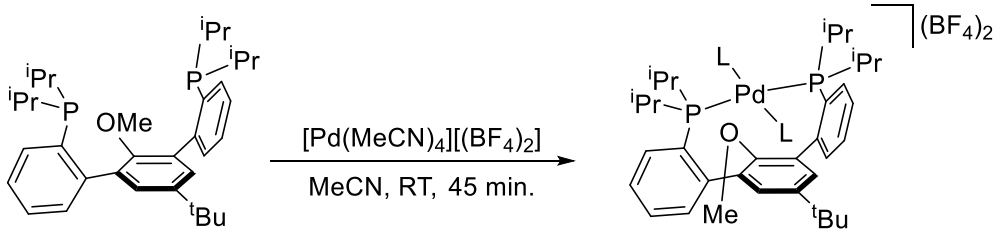
1b **32b**

Synthesis of [1,3-bis(2'-diisopropylphosphinophenyl)-5-tert-butyl-2-methoxybenzene]palladium(II) chloride (33a).



1a **33a**

Synthesis of [(1,3-bis(2'-diisopropylphosphinophenyl)-5-tert-butyl-2-methoxybenzene)palladium(II) bisacetontrile][tetrafluoroborate] (34a).

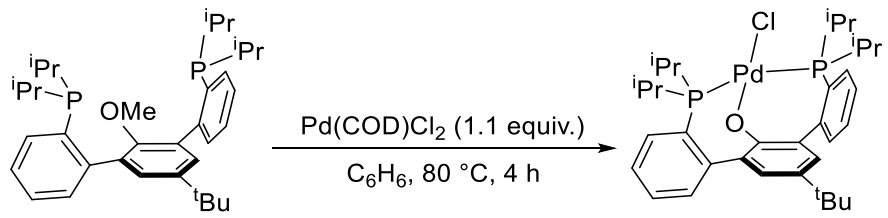


1a

L: MeCN

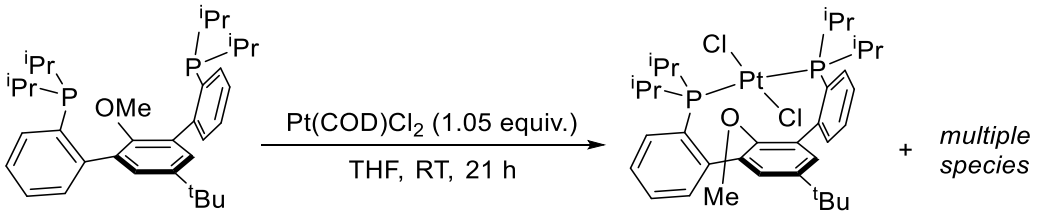
34a

Synthesis of [2,6-bis(2'-diisopropylphosphinophenyl)-4-tert-butyl-phenoxide]palladium(II)chloride (35a).



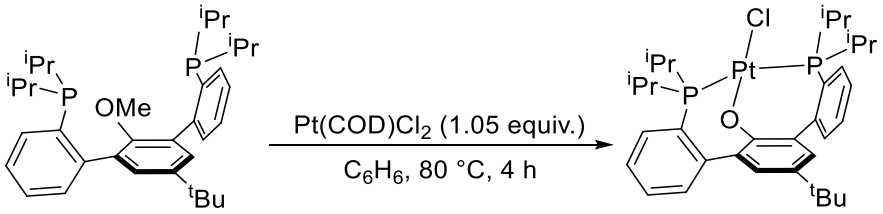
1a **35a**

Synthesis of [1,3-bis(2'-diisopropylphosphinophenyl)-5-tert-butyl-2-methoxybenzene]platinum(II) chloride (36a).



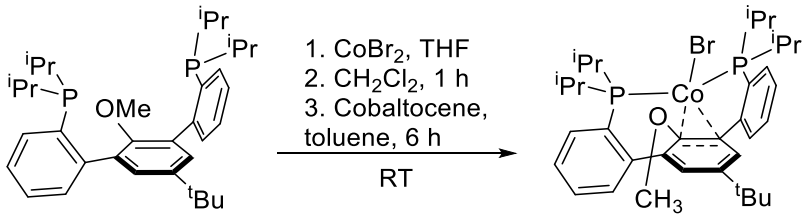
1a **36a**

Synthesis of [2,6-bis(2'-diisopropylphosphinophenyl)-4-tert-butyl-phenoxide]platinum(II)chloride (37a).



1a **37a**

Synthesis of [1,3-bis(2'-diisopropylphosphinophenyl)-5-tert-butyl-2-methoxybenzene]cobalt(I) bromide (37a).



1a **38a**

II. Crystallographic Data

Table S1. Crystal and refinement data for 5a, 8a, 19a, 26a.

	Complex **5a**	Complex **8a**	Complex **19a**	Complex **26a**
Empirical formula	$C_{35}H_{50}OP_2Pd_{0.69}$	$C_{35}H_{50}OP_2Pt$	$C_{34}H_{48}ClP_2Rh$	$C_{37.5}H_{54}ClOP_2Rh$
Formula weight (g/mol)	622.11	743.78	657.02	721.10
T (K)	100	100(2)	100(2)	100
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
a (Å)	11.2133(4)	15.5042(7)	21.062(8)	26.5795(9)
b (Å)	15.3800(6)	15.5042(7)	10.977(4)	23.0419(8)
c (Å)	19.1855(8)	11.8599(8)	29.071(11)	24.1024(8)
α (deg)	90	90	90	90
β (deg)	92.738(2)	90	105.84(2)	103.6640(10)
γ (deg)	90	120	90	90
V (Å^3)	3305.0(2)	2468.9(2)	6466(4)	14343.5(8)
Z	4	3	8	16
Cryst. syst.	monoclinic	hexagonal	monoclinic	Monoclinic
Space group	$P2_1/n$	$P3_1$	$P2_1/c$	Cc
ρ_{calcd}g (cm^3)	1.250	1.501	1.350	1.336
2 σ range (deg)	3.4 to 77.54	4.458 to 87.8	3.986 to 57.058	4.506 to 79.662
Crystal size/mm	0.28 x 0.25 x 0.07	0.28 × 0.26 × 0.14	0.28 × 0.13 × 0.05	0.24 x 0.19 x 0.06
μ (mm^{-1})	0.520	4.385	0.731	0.668
GOF	1.211	0.980	1.816	1.009
R1, wR2 (I> 2σ (I))	0.0674, 0.1917	0.0234, 0.0400	0.0699, 0.0808	0.0639, 0.0915

Table S2. Crystal and refinement data for 28a, 32b, 34a, 38a.

	Complex **28a**	Complex **32b**	Complex **34a**	Complex **38a**
Empirical formula	$C_{35}H_{47}IrO_2P_2$	$C_{32}H_{44}ClNNiOP_2$	$C_{41}H_{59}B_2F_8N_3OP_2Pd$	$C_{38}H_{56}BrCoOP_2$
Formula weight (g/mol)	753.87	614.78	951.87	729.60
T (K)	100(2)	100(2)	100(2)	100.0(2)
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
a (Å)	15.4739(5)	17.0566(7)	12.3085(5)	18.7532(9)
b (Å)	15.4739(5)	10.9300(4)	17.2927(7)	12.5873(6)
c (Å)	11.8879(5)	33.5079(14)	21.7237(9)	15.6898(7)
α (deg)	90	90	82.133(2)	90
β (deg)	90	97.838(2)	86.587(2)	96.330(3)
γ (deg)	120	90	86.032(2)	90
V (Å^3)	2465.10(15)	6188.5(4)	4563.5(3)	3681.0(3)
Z	3	8	4	4
Cryst. syst.	hexagonal	monoclinic	triclinic	monoclinic
Space group	$P3_1$	$P2_1/n$	P-1	$P2_1/1$
ρ_{calcd}g (cm^3)	1.523	1.320	1.385	1.317
2 σ range (deg)	4.58 to 106.76	3.92 to 60.3	1.894 to 77.678	3.904 to 74.614
Crystal size/mm	0.40 × 0.27 × 0.23	0.18 × 0.16 × 0.08	0.42 × 0.34 × 0.15	0.44 × 0.28 × 0.05
μ (mm^{-1})	4.188	0.842	0.544	1.666
GOF	0.907	1.050	1.044	0.980
R1, wR2 (I> 2σ (I))	0.0249, 0.0404	0.0570, 0.1043	0.0548, 0.1289	0.0392, 0.0892

III. Nuclear Magnetic Resonance Data

Figure S1. ^{1}H NMR spectrum of **5a** in C_6D_6.

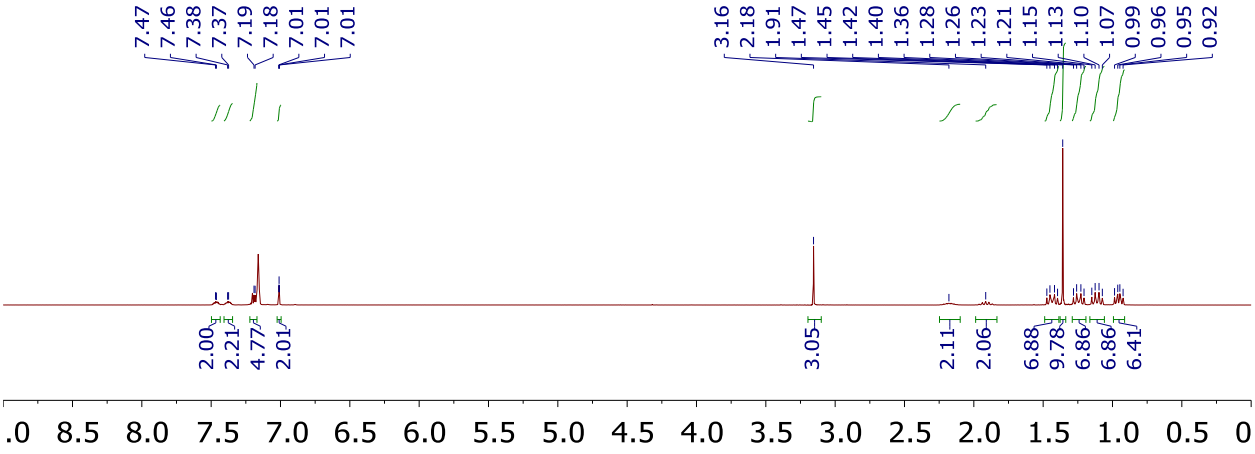


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of **5a** in C_6D_6.

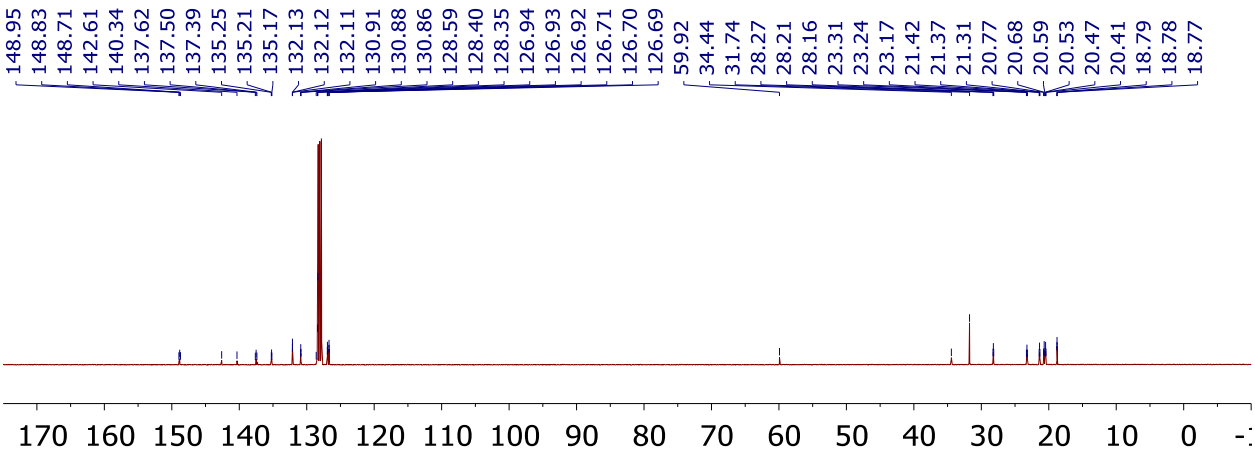


Figure S3. $^{31}P\{^{1}H\}$ NMR spectrum of **5a** in C_6D_6.

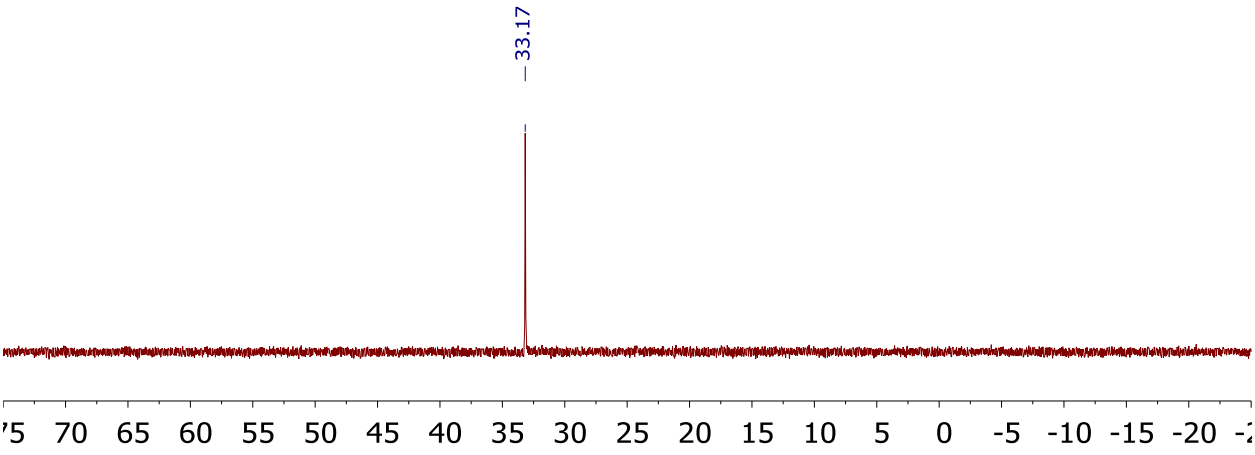


Figure S4. ^{1}H NMR spectrum of **6a** in C_6D_6.

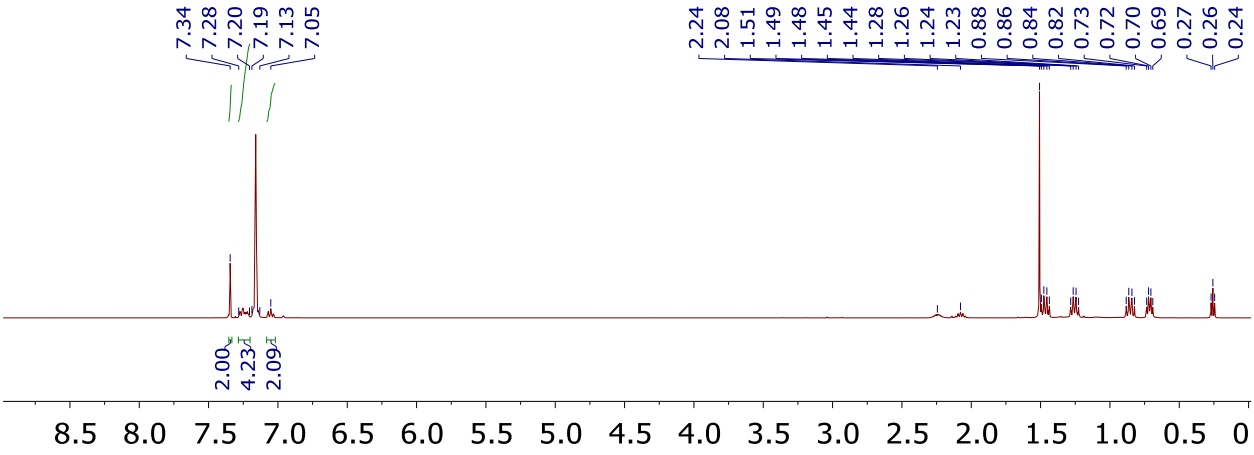


Figure S5. $^{13}C\{^{1}H\}$ NMR spectrum of **6a** in C_6D_6.

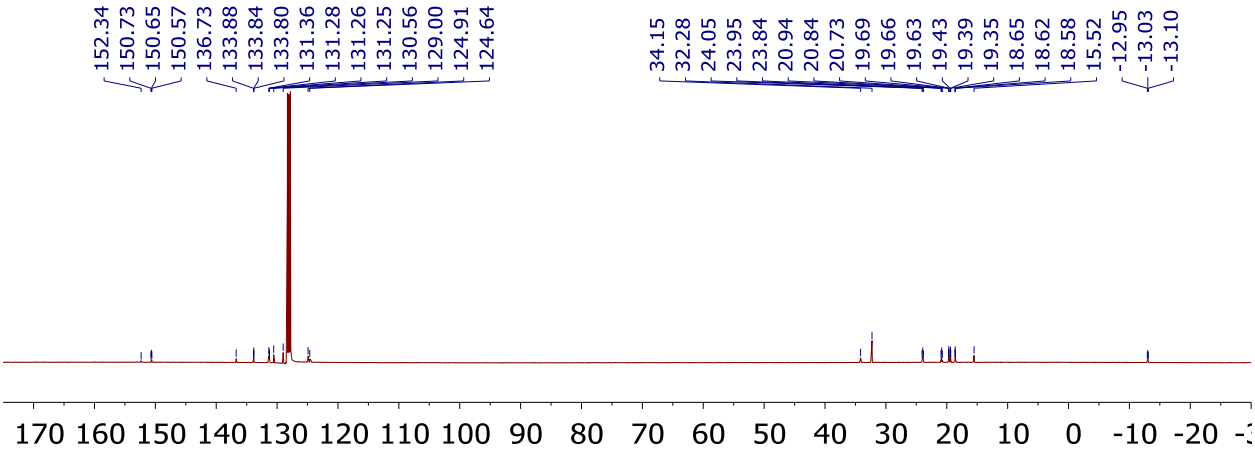


Figure S6. $^{31}P\{^{1}H\}$ NMR spectrum of **6a** in C_6D_6.

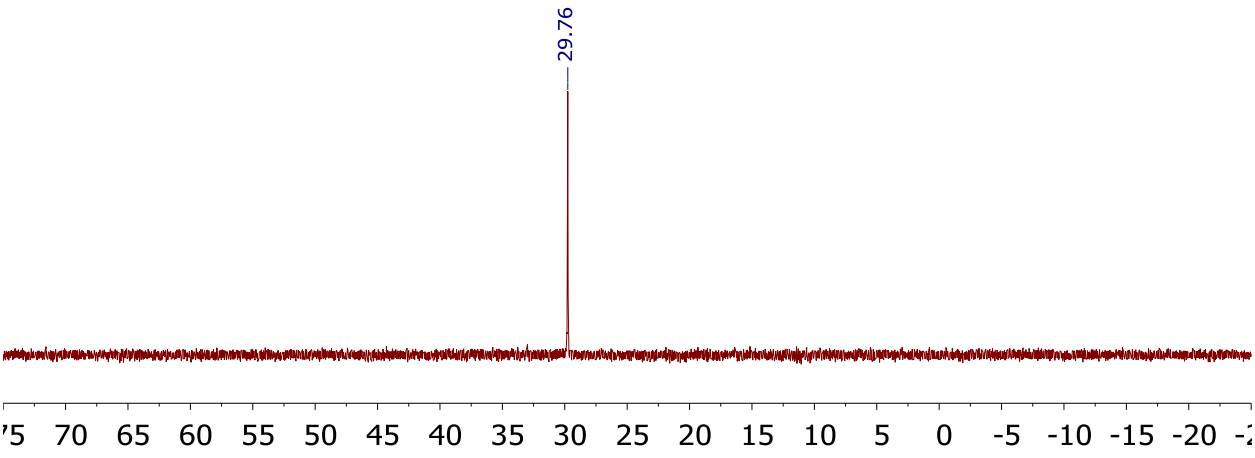


Figure S7. ^{1}H NMR spectrum of **7a** in C_6D_6.

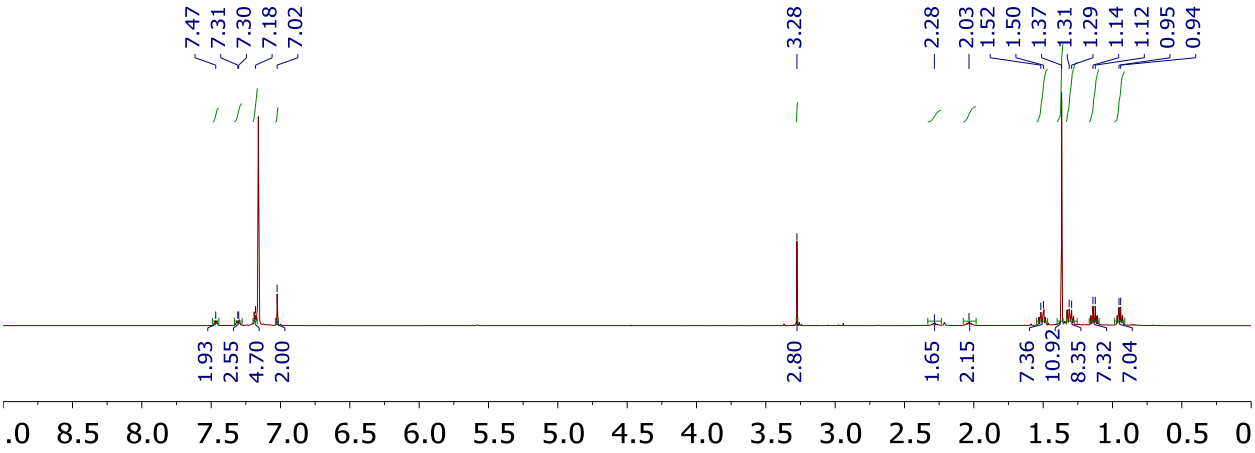


Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum of **7a** in C_6D_6.

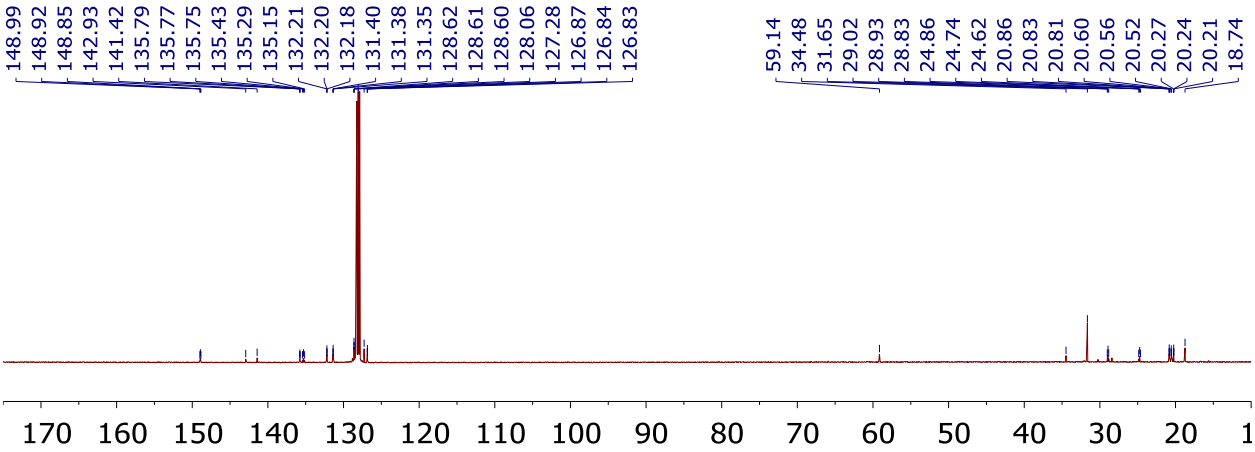


Figure S9. $^{31}P\{^{1}H\}$ NMR spectrum of **7a** in C_6D_6.

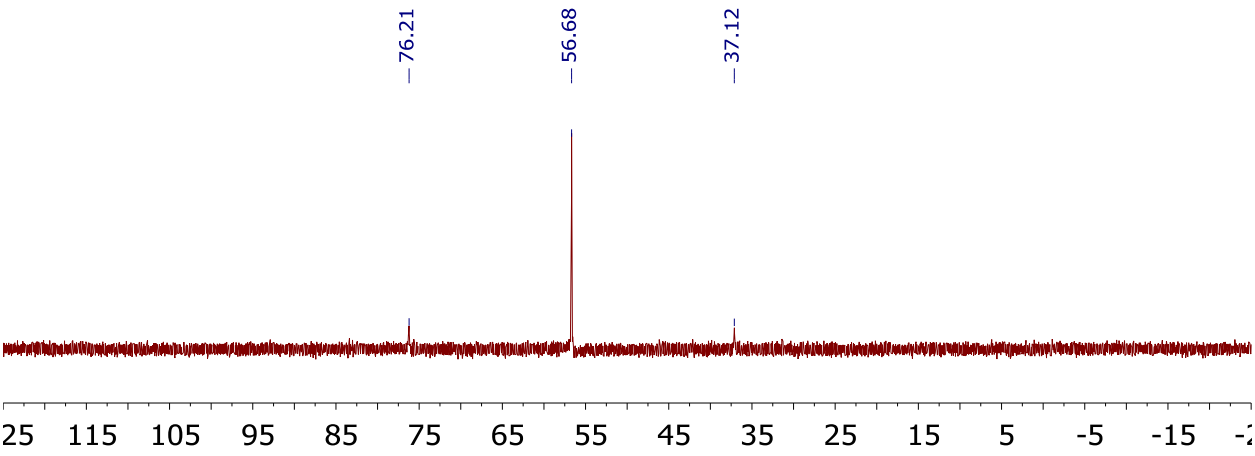


Figure S10. ^{1}H NMR spectrum of **8a** in C_6D_6.

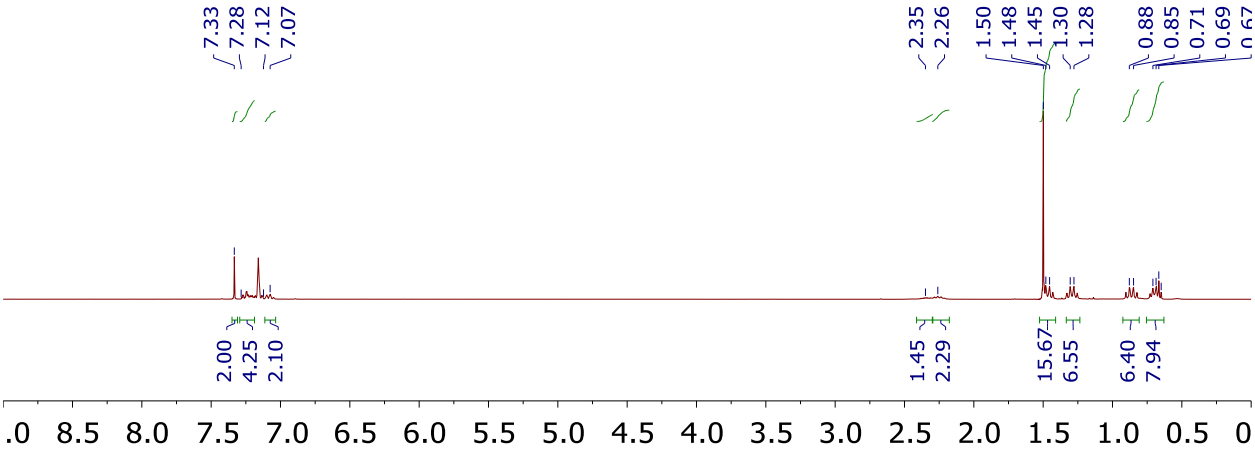


Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum of **8a** in C_6D_6.

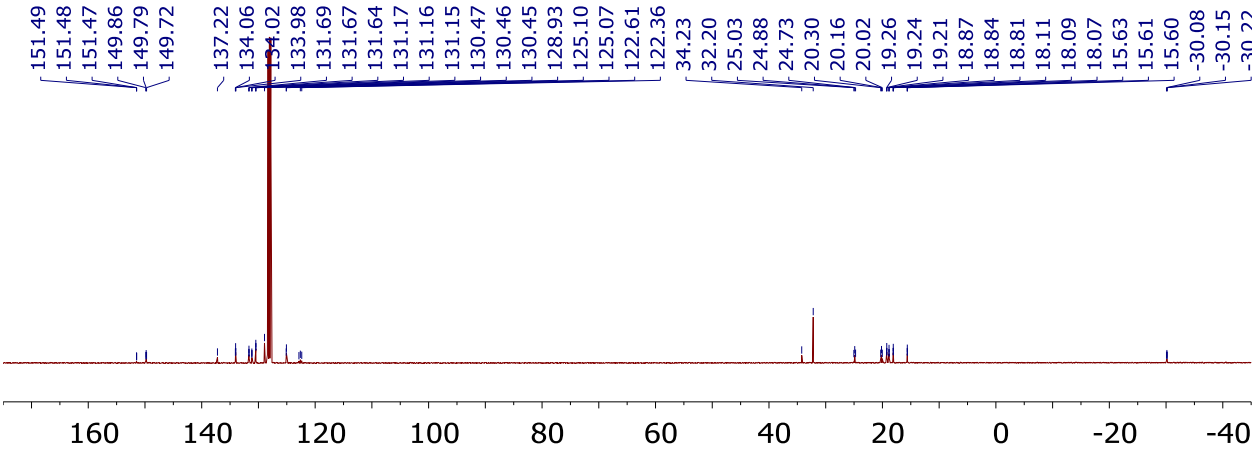


Figure S12. $^{31}P\{^{1}H\}$ NMR spectrum of **8a** in C_6D_6.

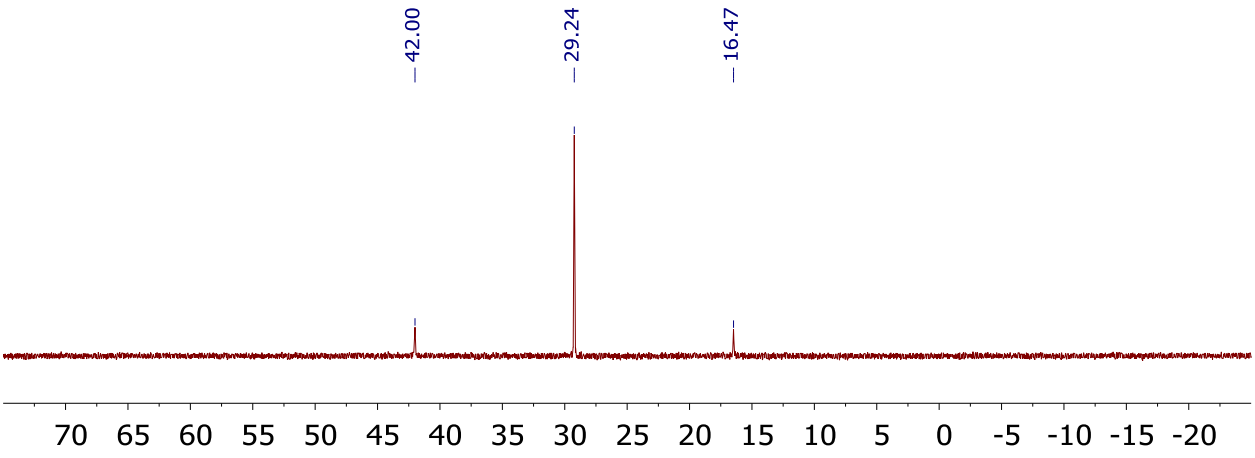


Figure S13. ^{1}H NMR spectrum of 5-(tert-butyl)-1,3-diiodo-2-(4-nitrophenoxy)benzene in $CDCl_3$.

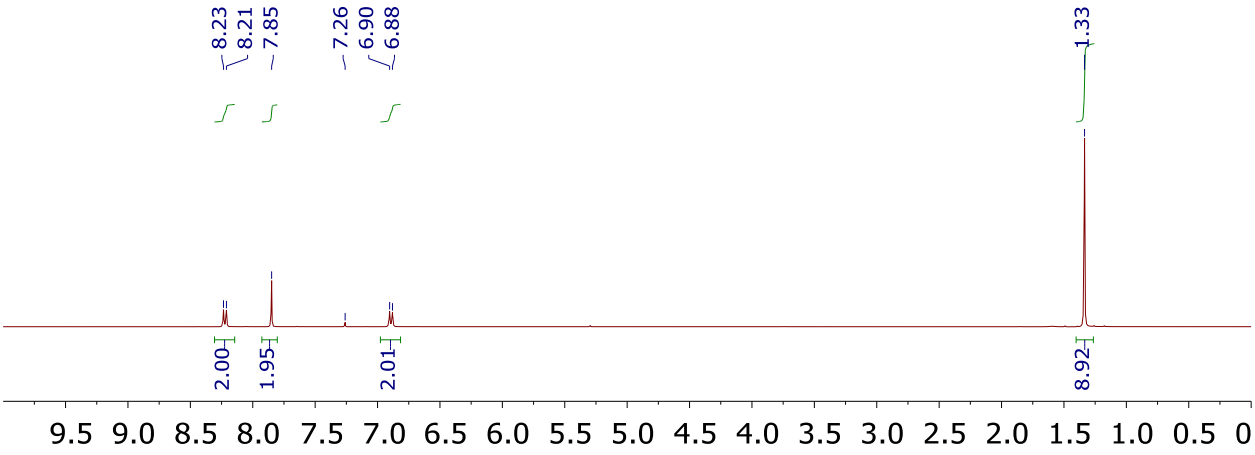


Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum of 5-(tert-butyl)-1,3-diiodo-2-(4-nitrophenoxy)benzene in $CDCl_3$.

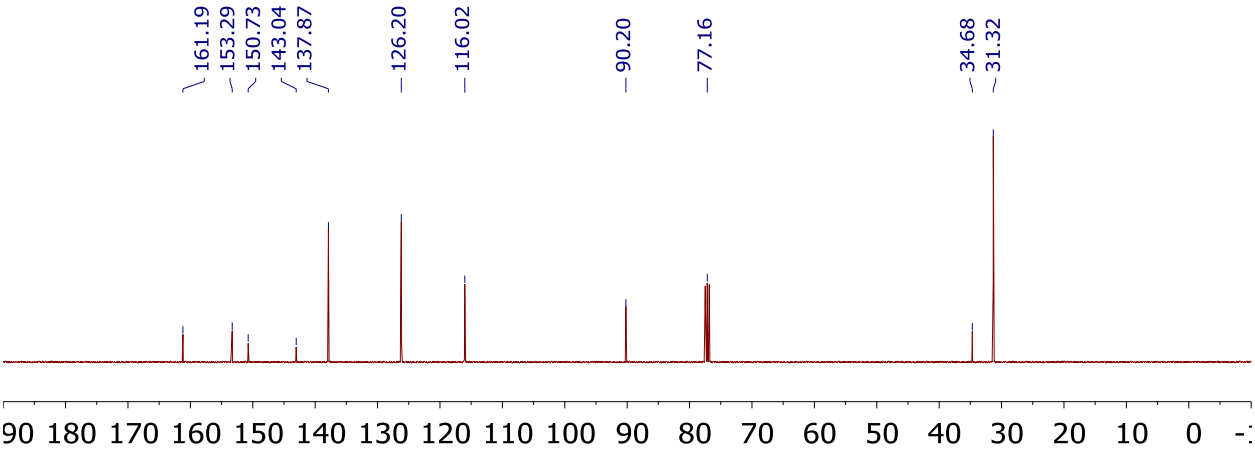


Figure S15. ^{1}H NMR spectrum of 1,3-bis(2'-bromophenyl)-2-(4'-nitrophenoxy)-5-tert-butyl-benzene in $CDCl_3$. Note: Residual CH_2Cl_2 present.

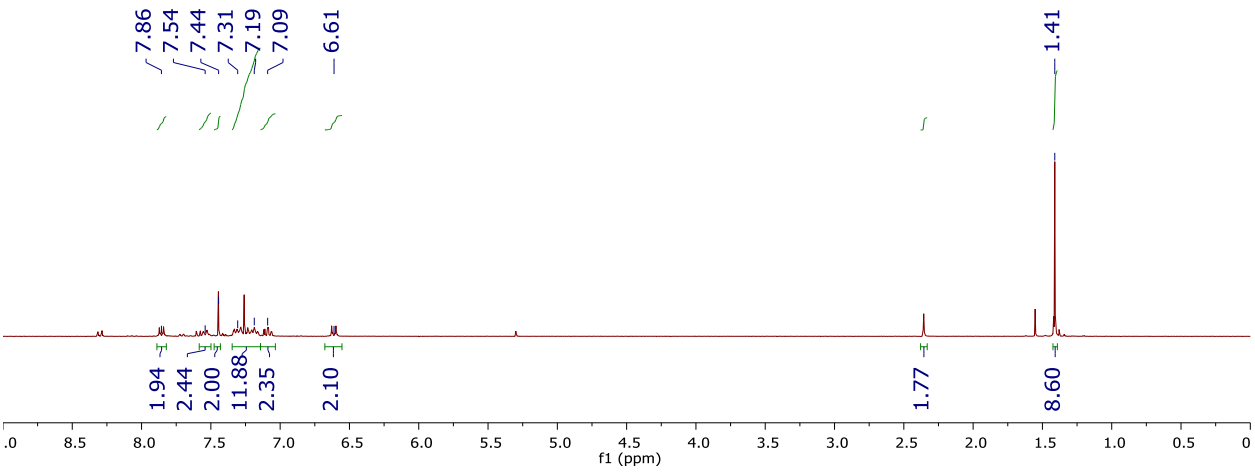


Figure S16. ^{1}H NMR spectrum of 1,3-bis(2'-bromophenyl)-2-(4'-aminophenoxy)-5-tert-butyl-benzene in $CDCl_3$. Note: Residual CH_2Cl_2 and Et_2O present.

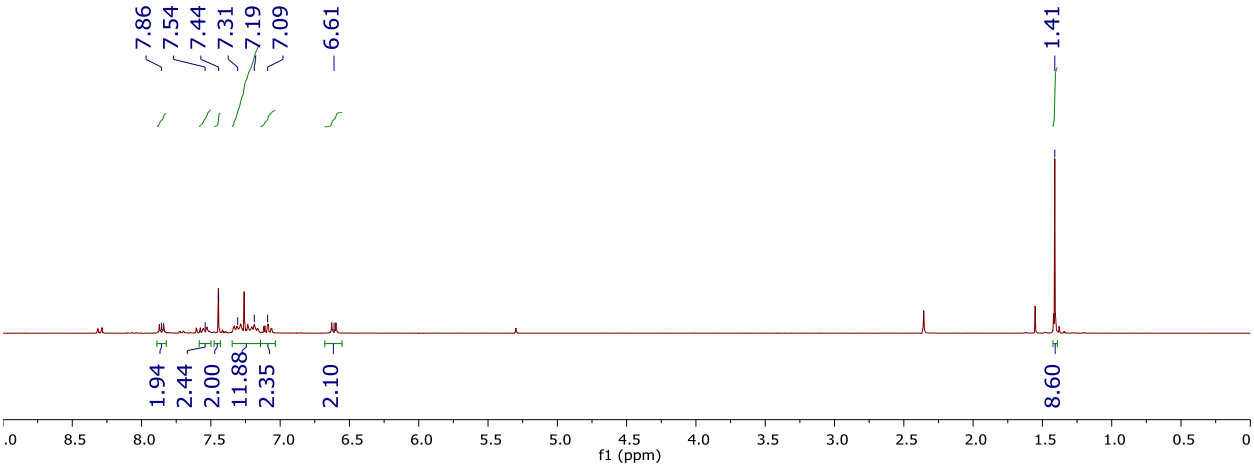


Figure S17. ^{1}H NMR spectrum of 1,3-bis(2'-bromophenyl)-2-(4'-dimethylaminophenoxy)-5-tert-butyl-benzene in C_6D_6. Note: Residual Et_2O present.

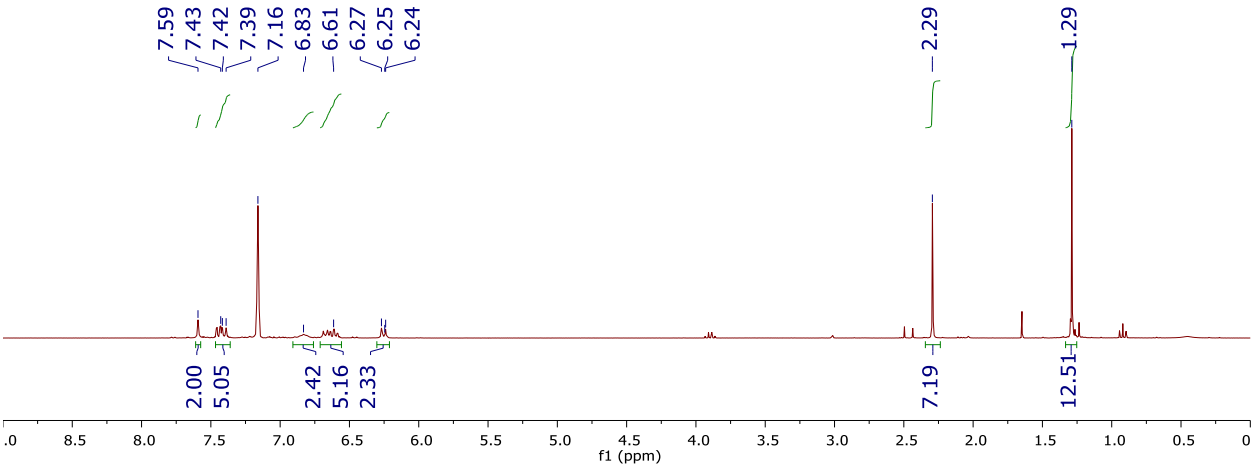


Figure S18. ^{1}H NMR spectrum of **1c** at 25 °C in C_6D_6.

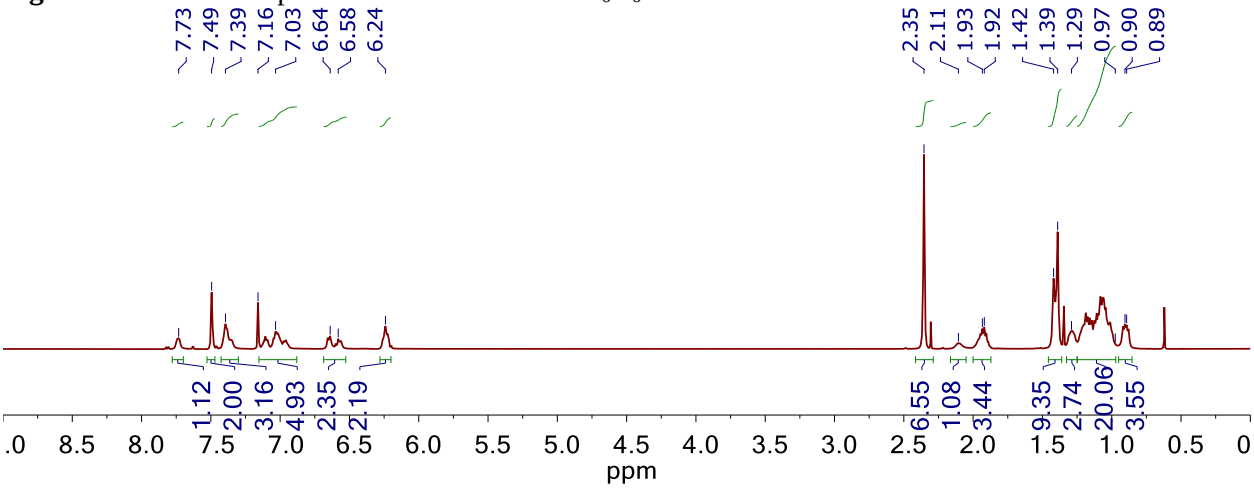


Figure S19. $^{13}C\{^{1}H\}$ NMR spectrum of **1c** at 25 °C in C_6D_6.

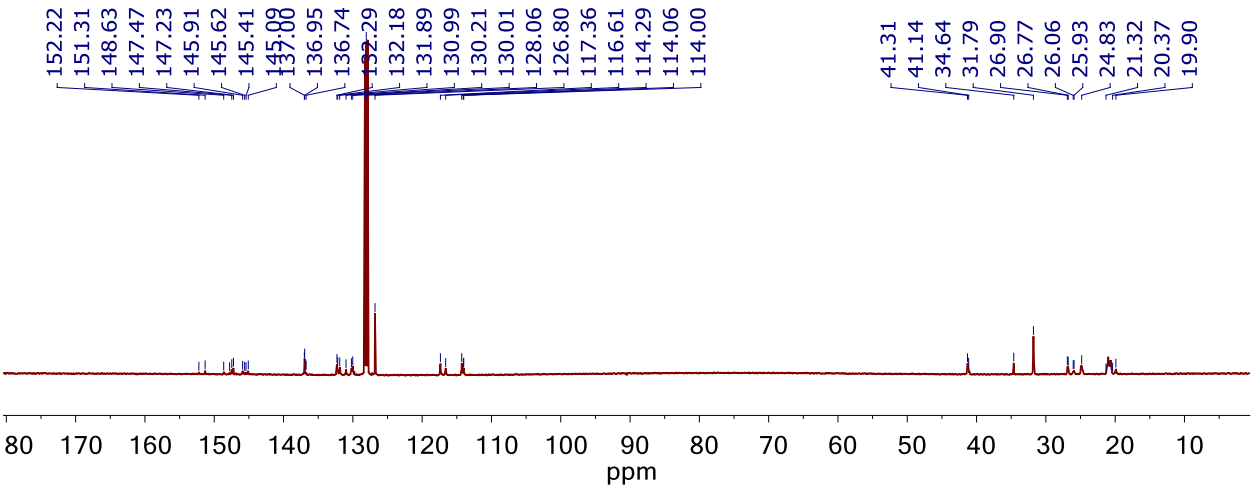


Figure S20. $^{31}P\{^{1}H\}$ NMR spectrum of **1c** at 25 °C in C_6D_6.

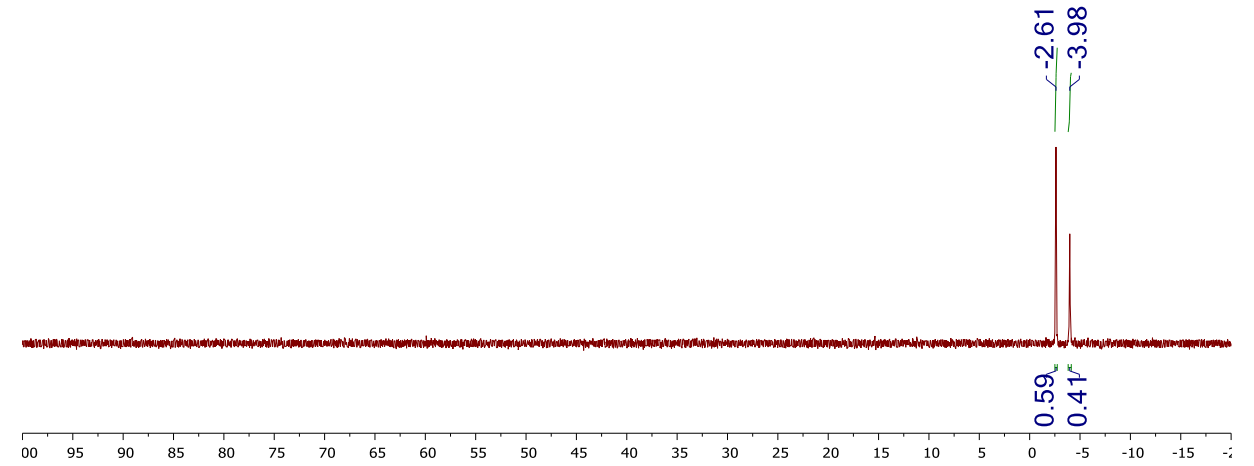


Figure S21. ^{1}H NMR spectrum of **1c** at 70 °C in C_6D_6.

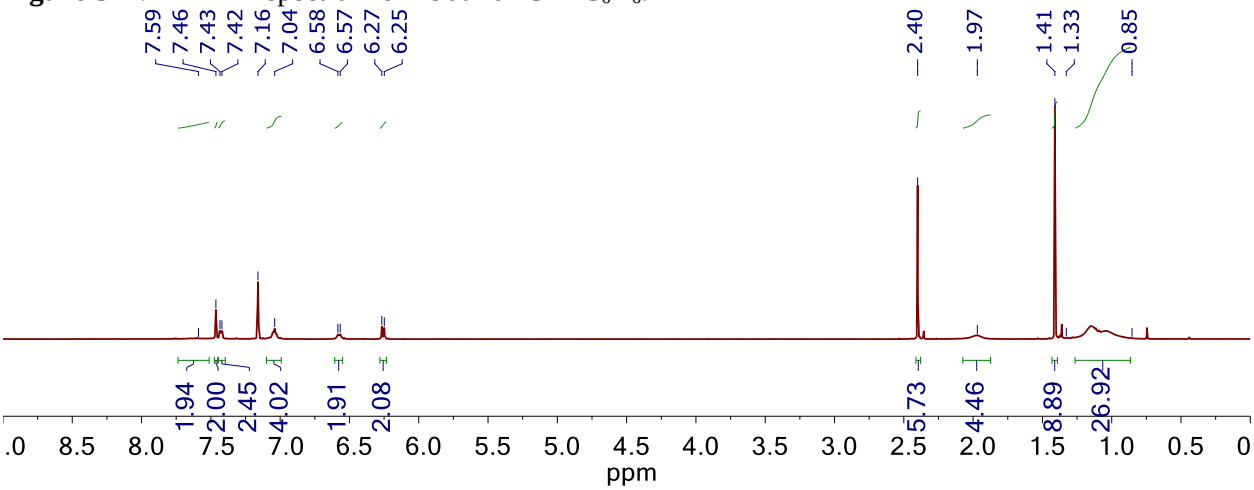


Figure S22. ^{1}H NMR spectrum of 1,3-bis(2'-bromophenyl)-2-phenoxy-5-tert-butyl-benzene in $CDCl_3$.

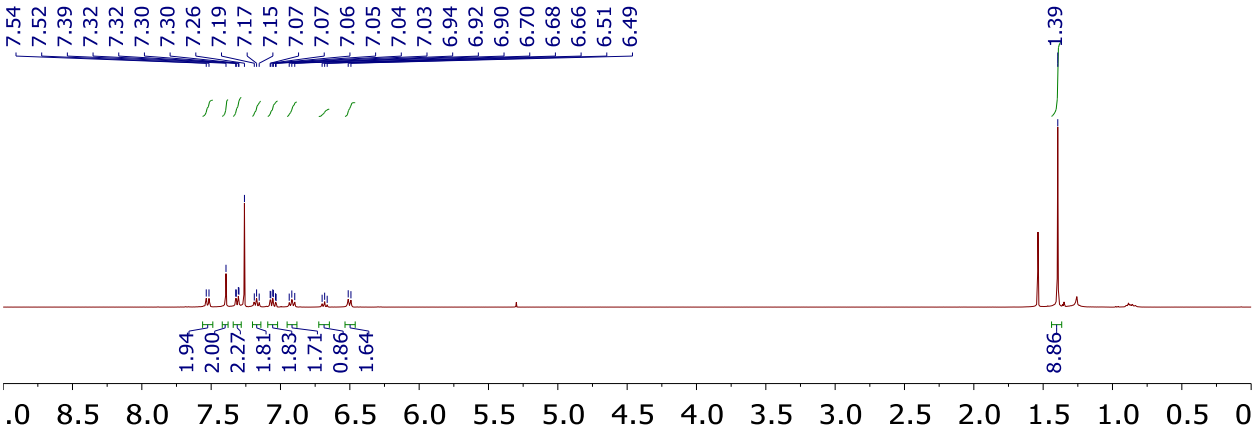


Figure S23. $^{13}C\{^{1}H\}$ NMR spectrum of 1,3-bis(2'-bromophenyl)-2-phenoxy-5-tert-butyl-benzene in $CDCl_3$.

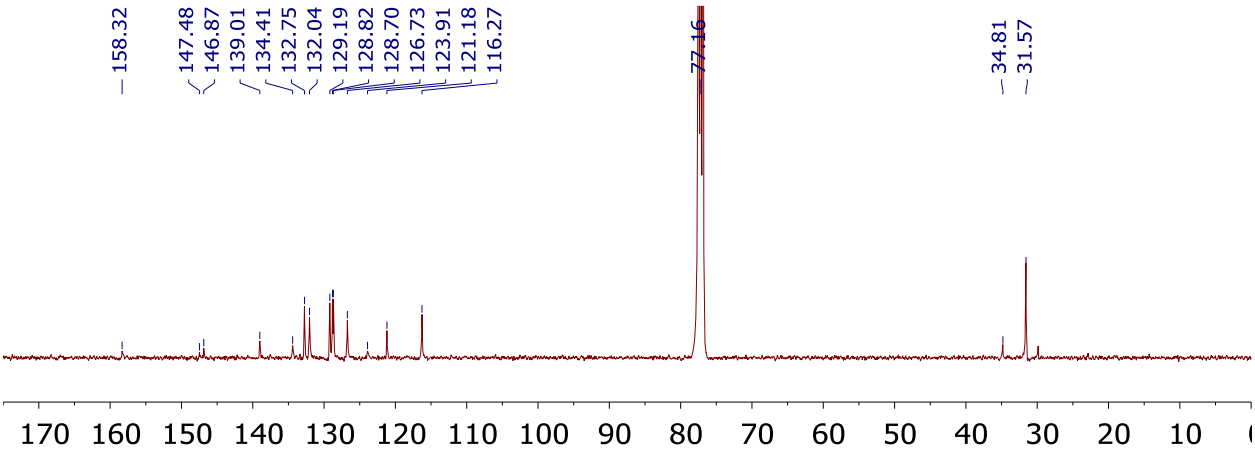


Figure S24. ^{1}H NMR spectrum of **1d** at 25 °C in $CDCl_3$.

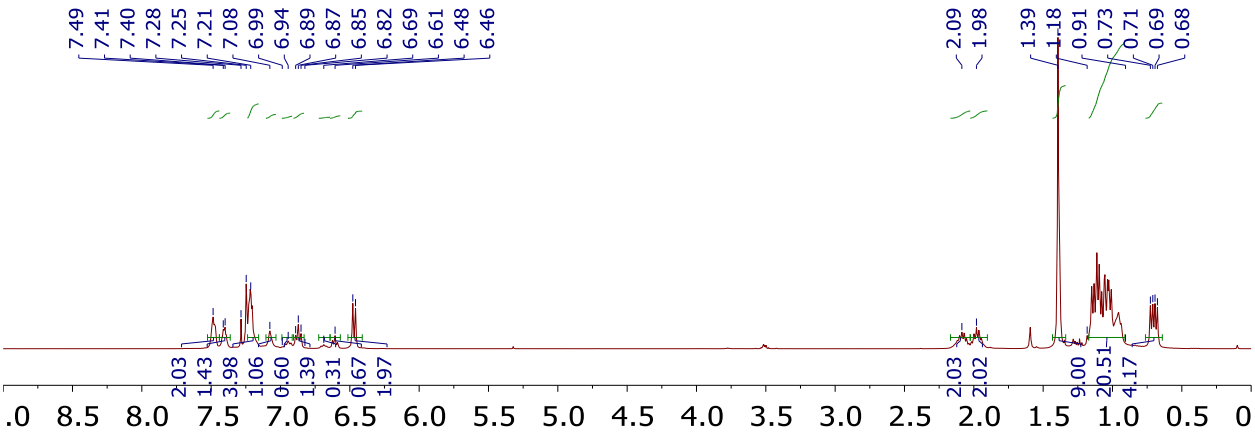


Figure S25. ^{1}H NMR spectrum of **1d** at 25 °C in C_6D_6.

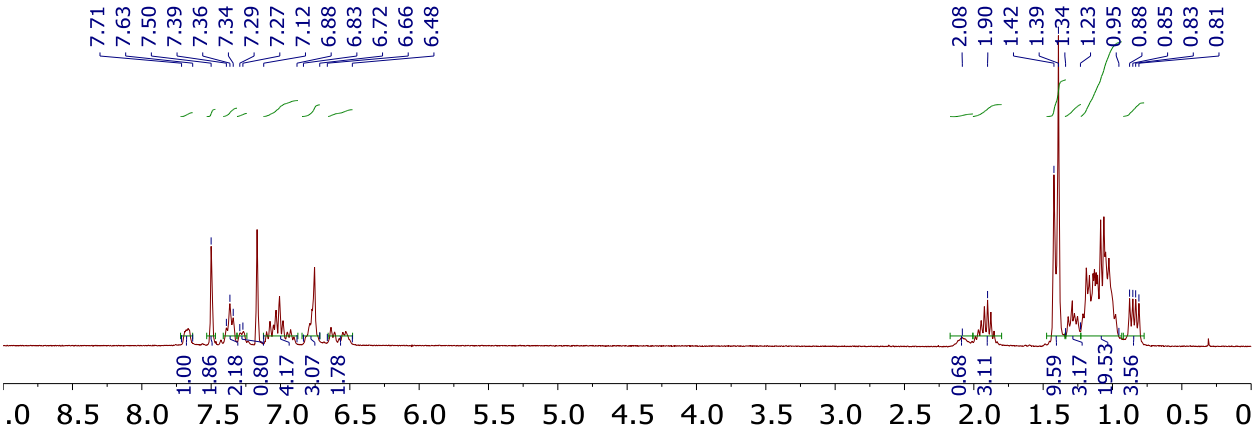


Figure S26. $^{13}C\{^{1}H\}$ NMR spectrum of **1d** at 25 °C in $CDCl_3$.

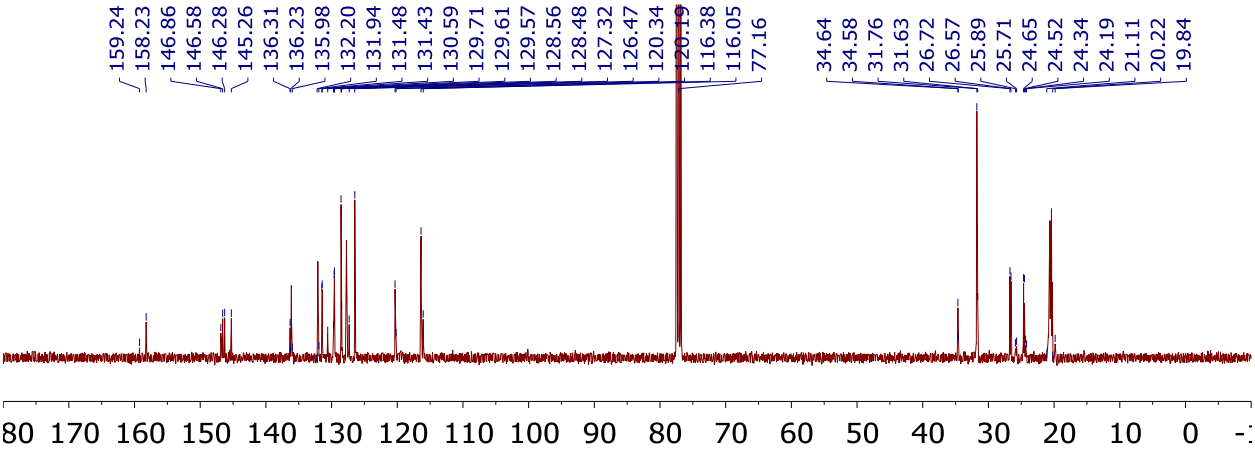


Figure S27. $^{31}P\{^{1}H\}$ NMR spectrum of **1d** at 25 °C in $CDCl_3$.

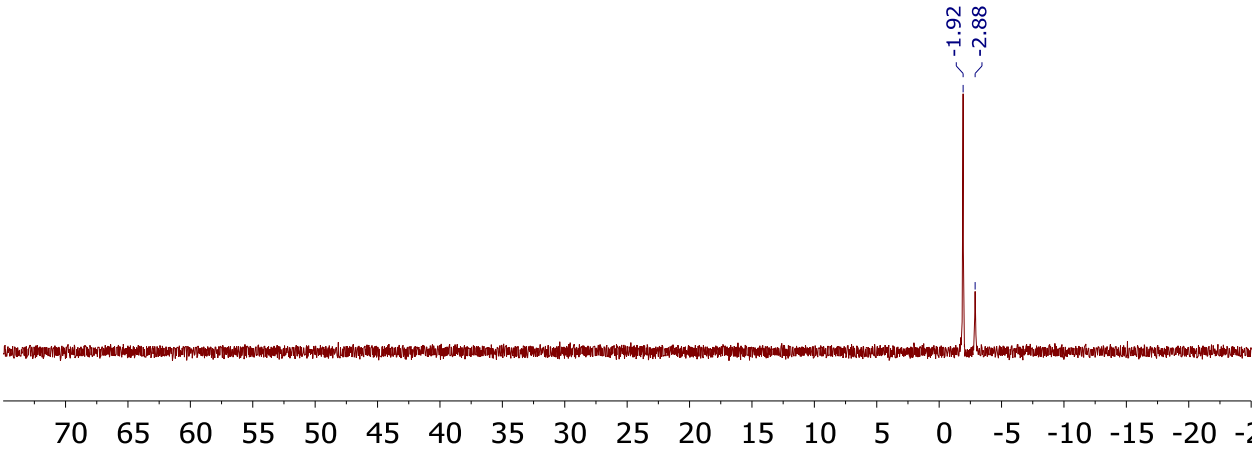


Figure S28. $^{31}P\{^{1}H\}$ NMR spectrum of **1d** at 25 °C in C_6D_6.

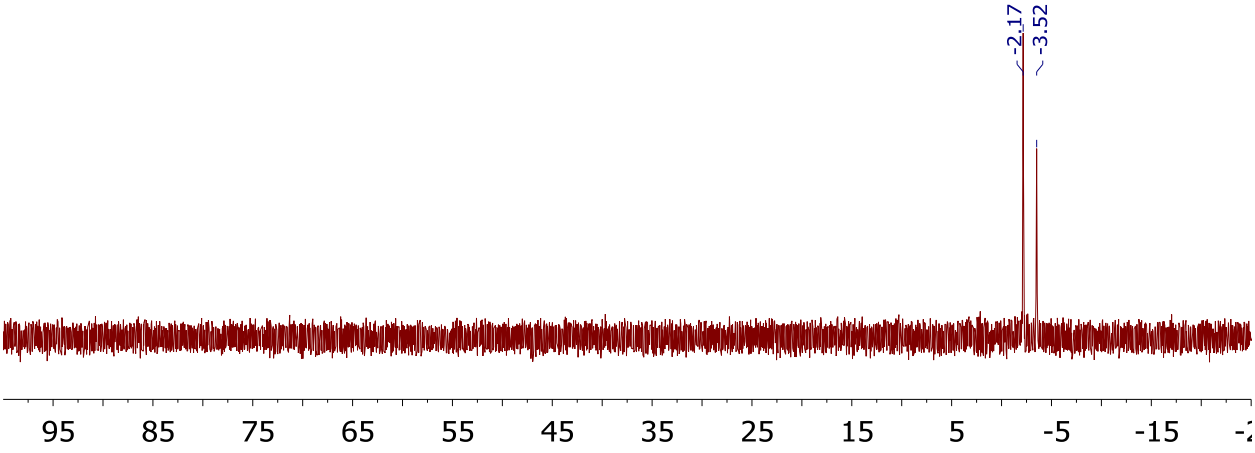


Figure S29. ^{1}H NMR spectrum of **1d** at 70 °C in C_6D_6.

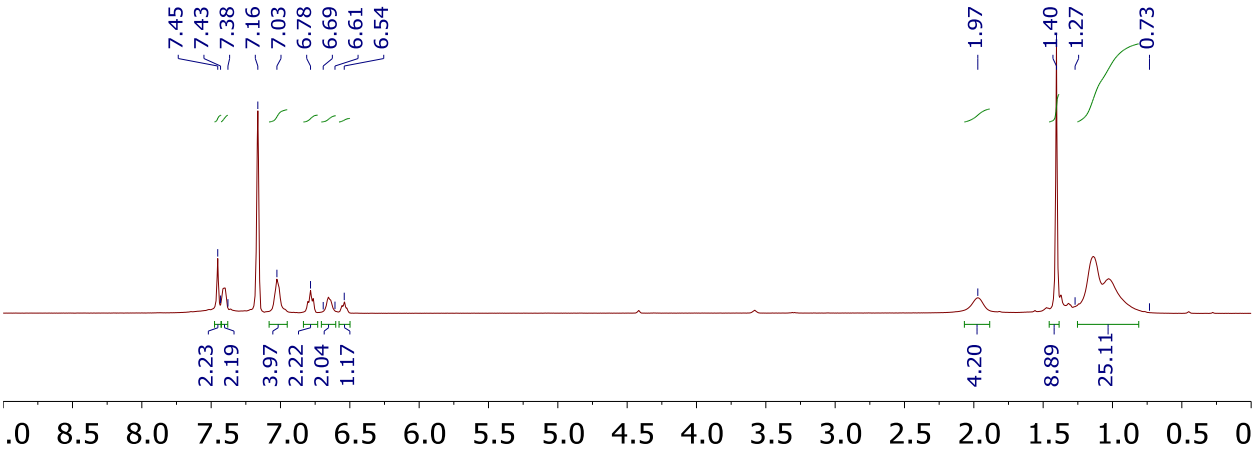


Figure S30. $^{13}C\{^{1}H\}$ NMR spectrum of **1d** at 70 °C in C_6D_6.

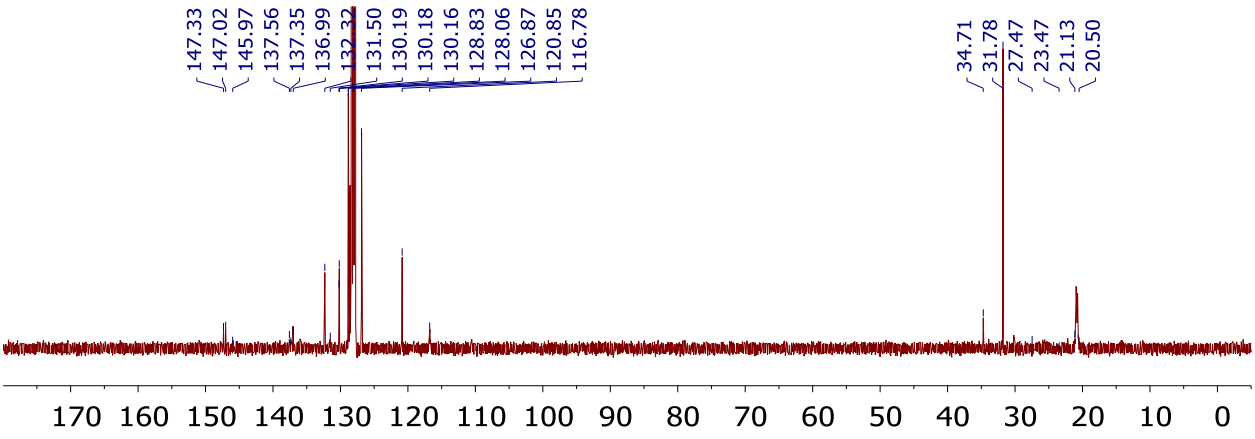


Figure S31. $^{31}P\{^{1}H\}$ NMR spectrum of **1d** at 70 °C in C_6D_6. (Note: Referenced to solvent lock.)

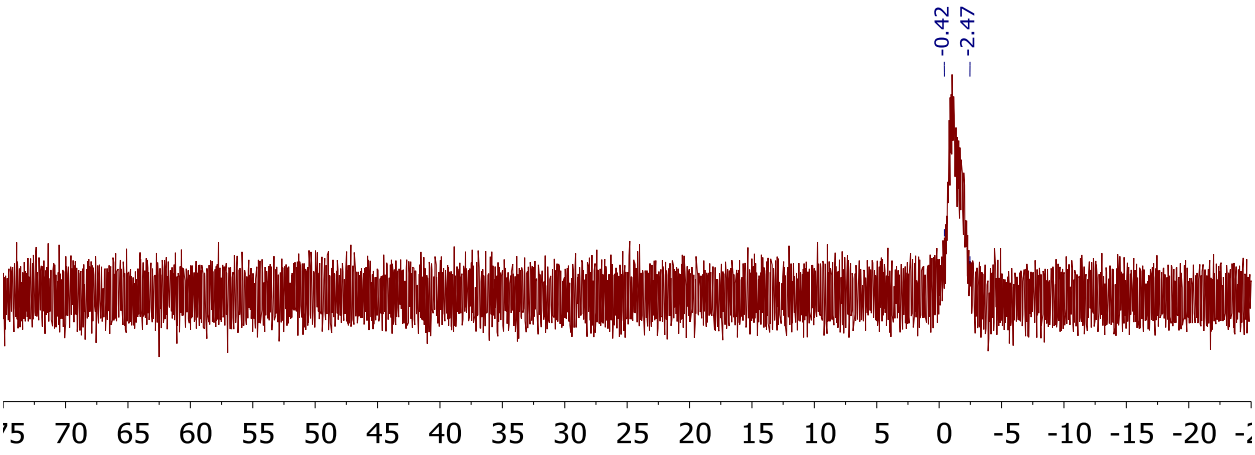


Figure S32. ^{1}H NMR spectrum of **10d** in C_6D_6.

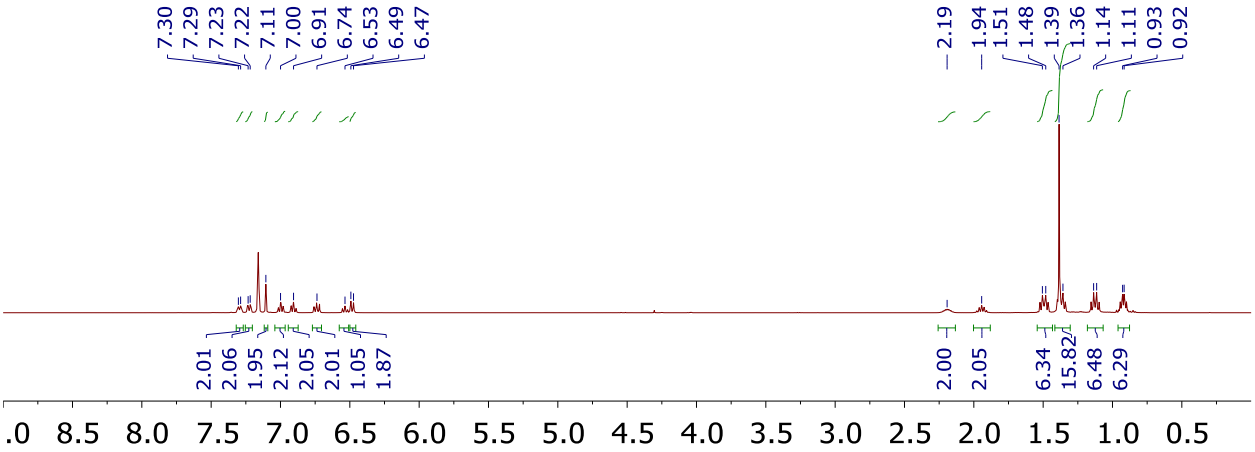


Figure S33. $^{13}C\{^{1}H\}$ NMR spectrum of **10d** in C_6D_6.

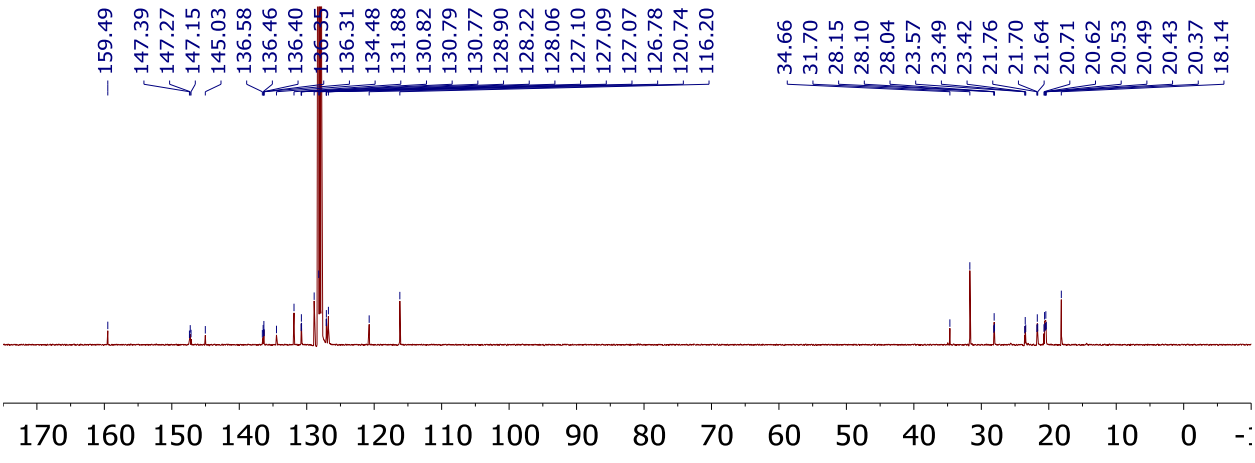


Figure S34. $^{31}P\{^{1}H\}$ NMR spectrum of **10d** in C_6D_6.

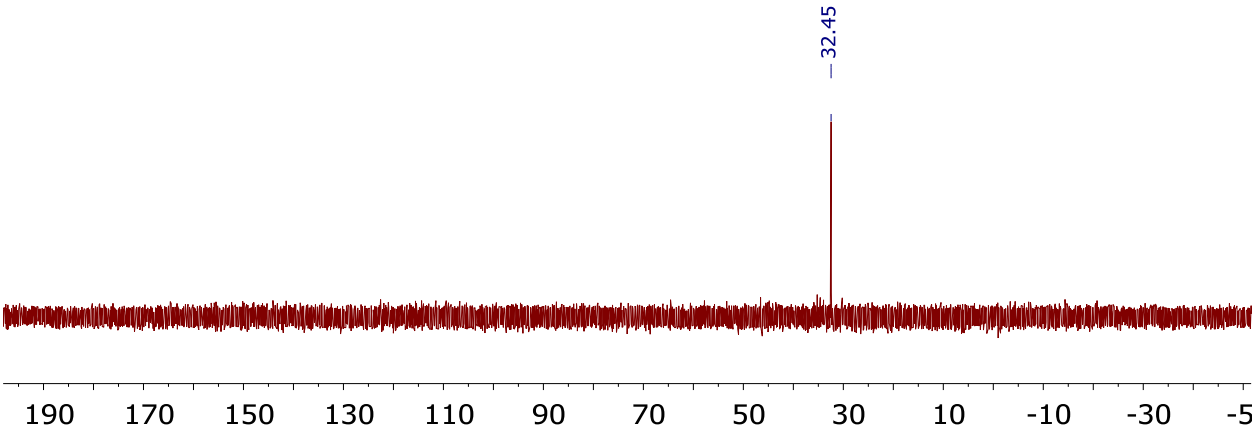


Figure S35. ^{1}H NMR spectrum of **11d** in C_6D_6.

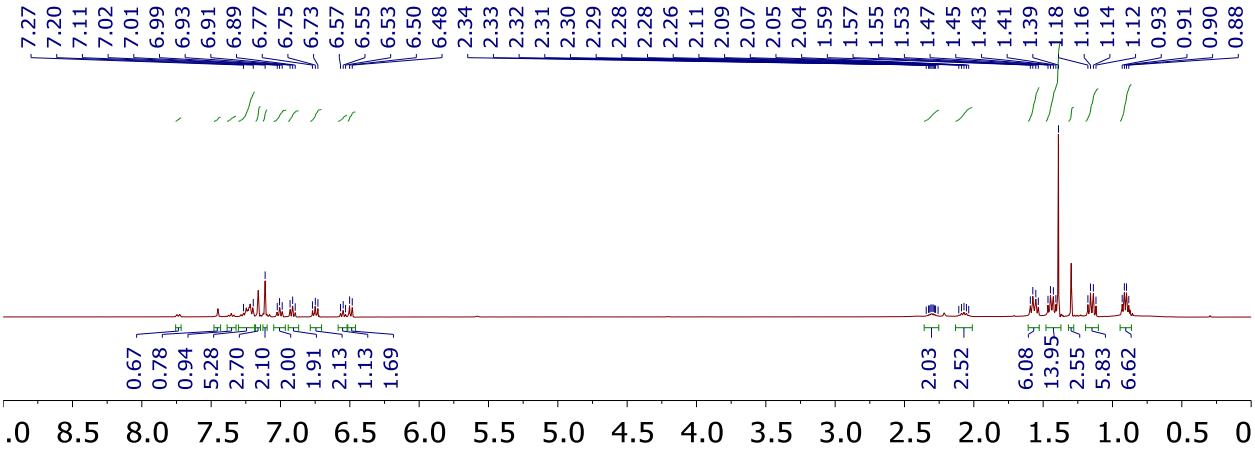


Figure S36. $^{13}C\{^{1}H\}$ NMR spectrum of **11d** in C_6D_6.

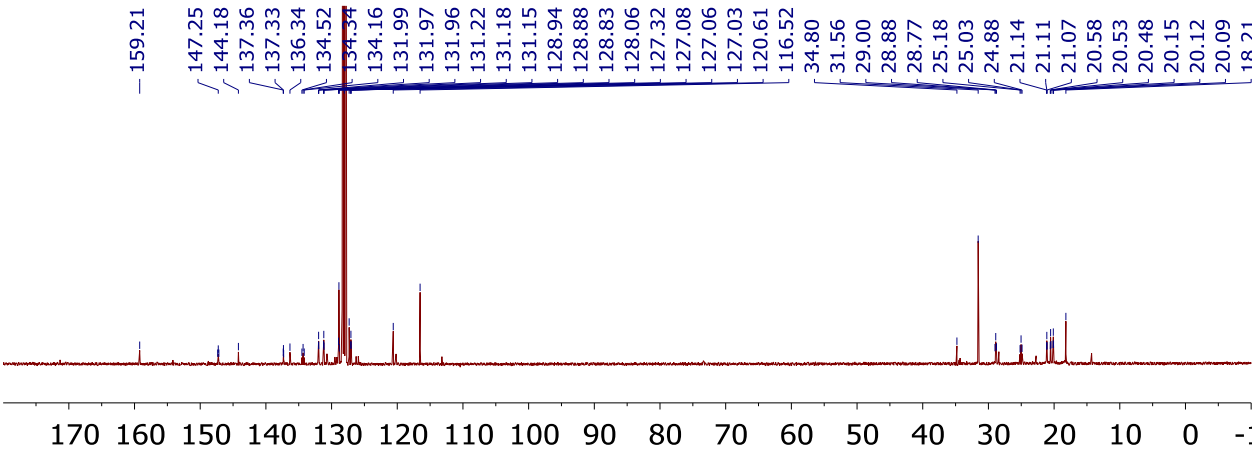


Figure S37. $^{31}P\{^{1}H\}$ NMR spectrum of **11d** in C_6D_6.

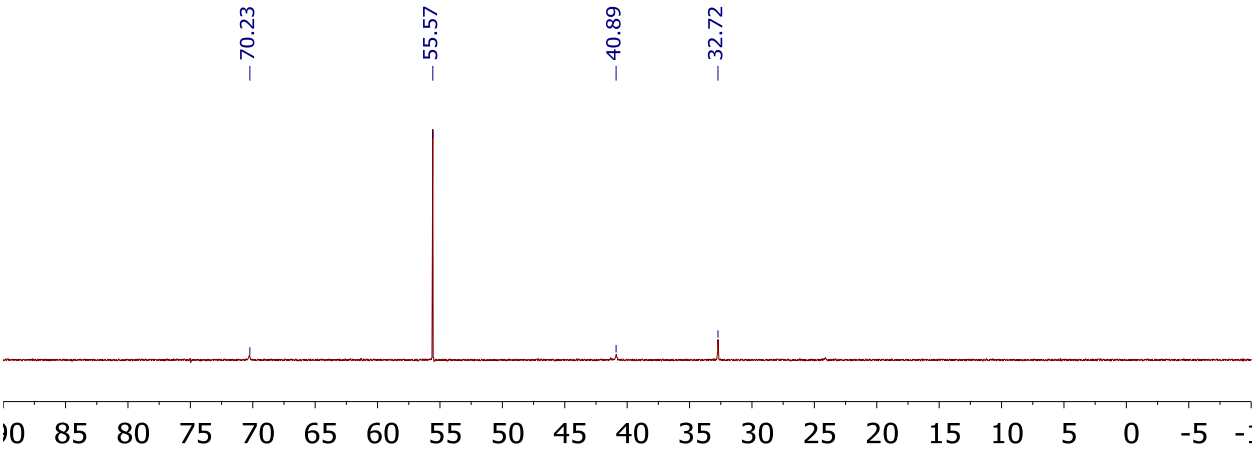


Figure S38. ^{1}H NMR spectrum of **12c** in C_6D_6.

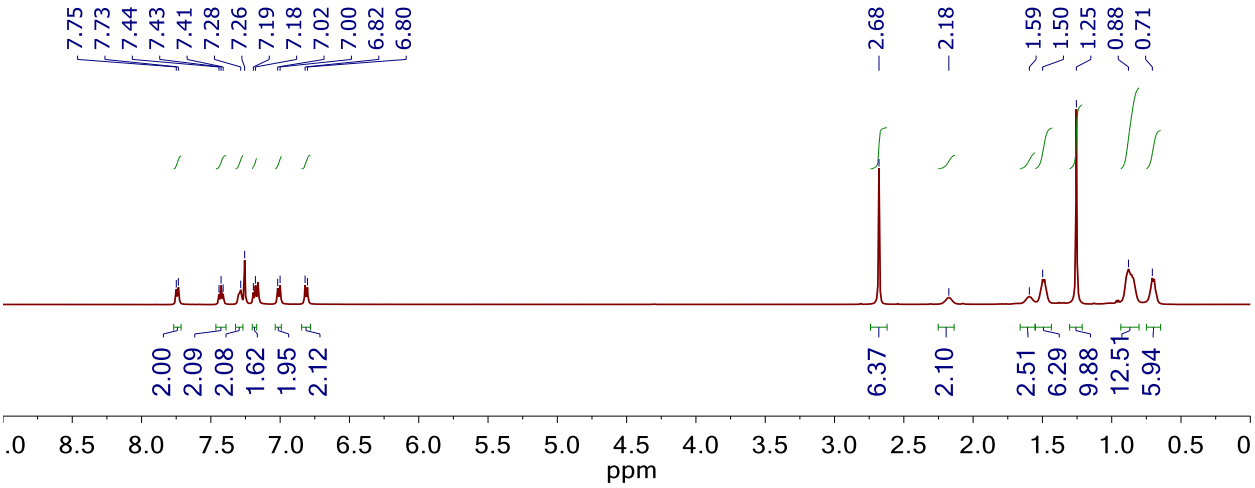


Figure S39. $^{13}C\{^{1}H\}$ NMR spectrum of **12c** in C_6D_6.

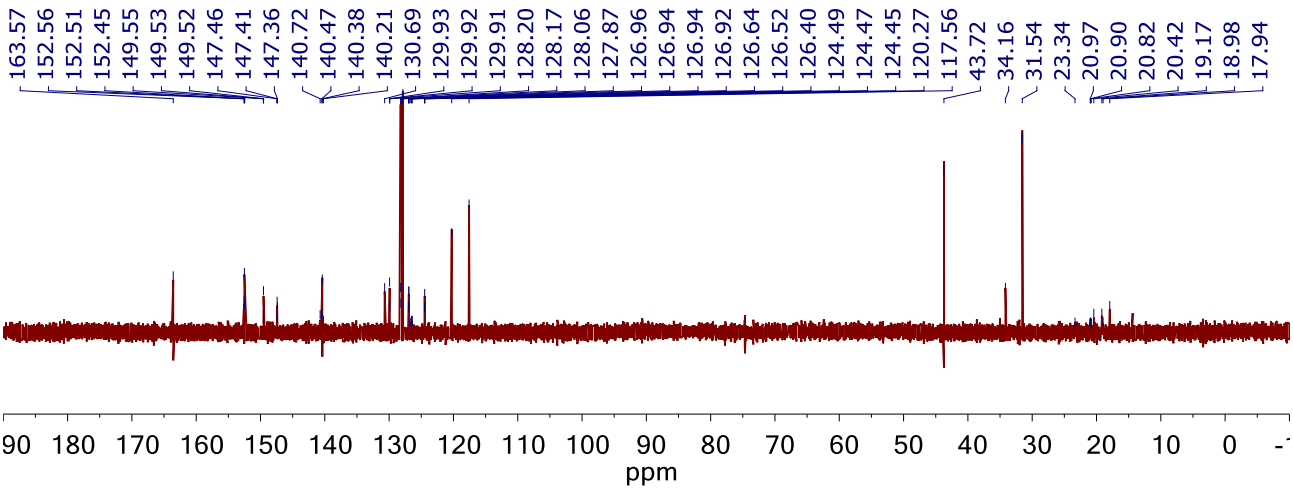


Figure S40. $^{31}P\{^{1}H\}$ NMR spectrum of **12c** in C_6D_6.

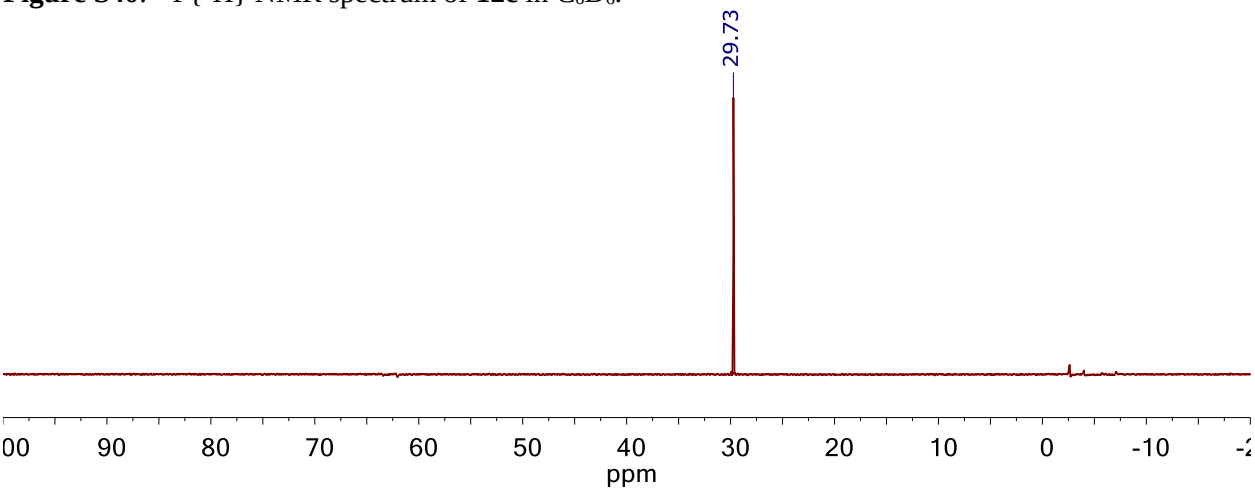


Figure S41. ^{1}H NMR spectrum of **13d** in C_6D_6.

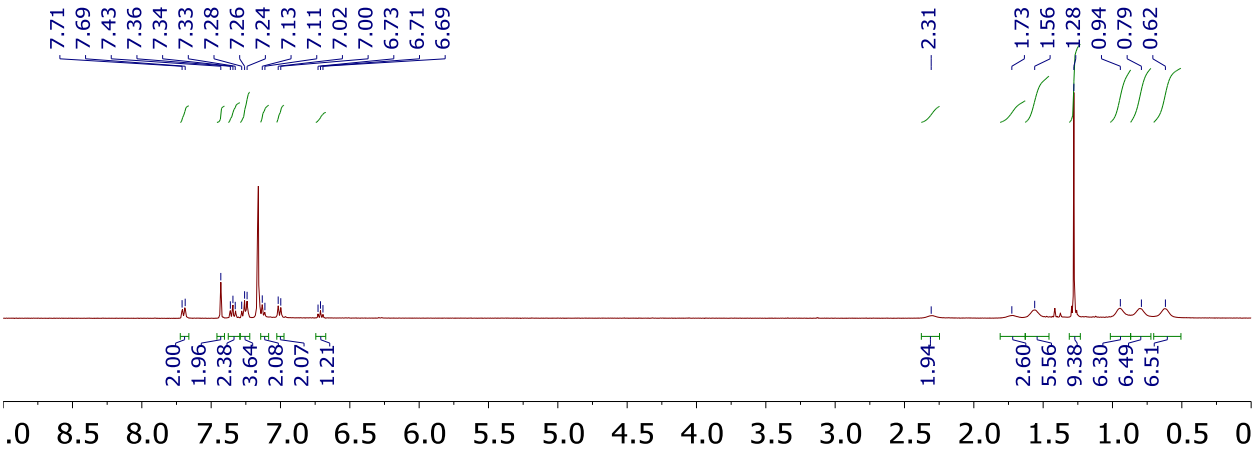


Figure S42. $^{13}C\{^{1}H\}$ NMR spectrum of **13d** in C_6D_6.

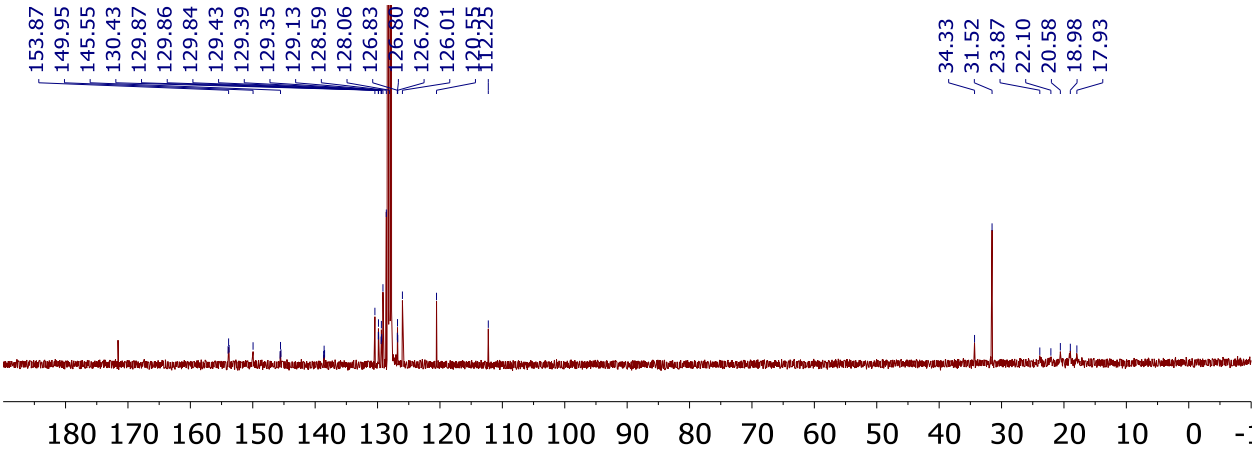


Figure S43. $^{31}P\{^{1}H\}$ NMR spectrum of **13d** in C_6D_6.

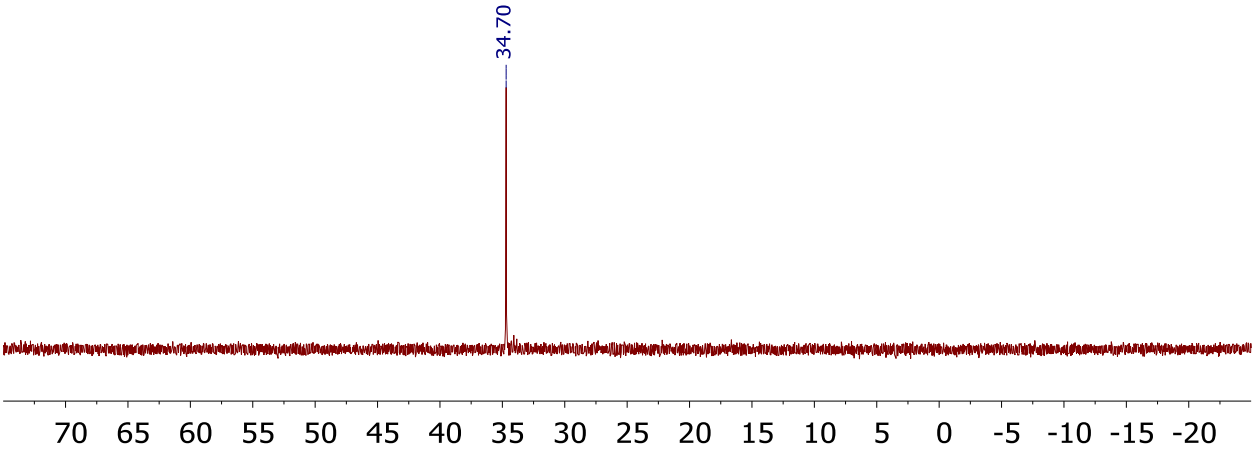


Figure S44. ^{1}H NMR spectrum of **14d** in C_6D_6.

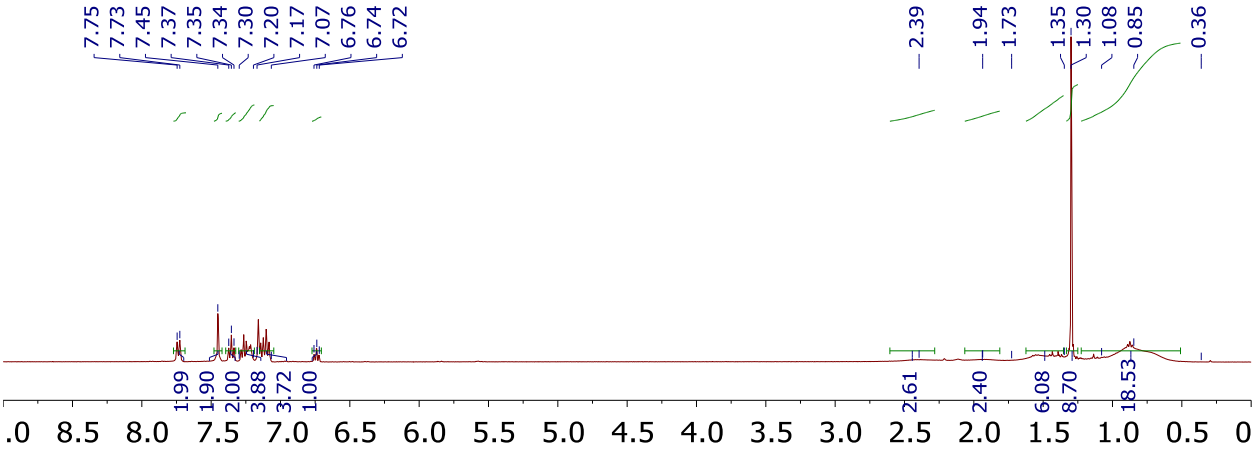


Figure S45. $^{13}C\{^{1}H\}$ NMR spectrum of **14d** in C_6D_6.

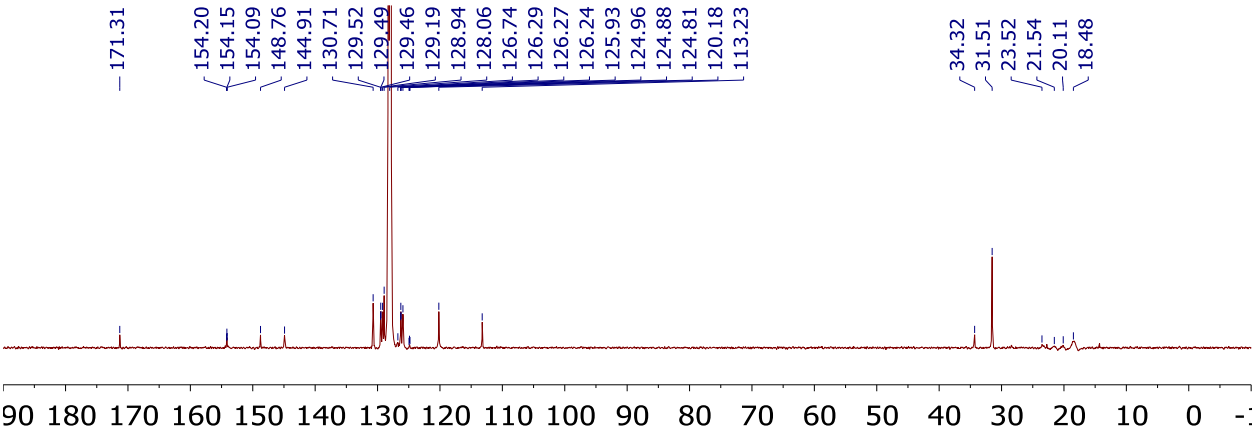


Figure S46. $^{31}P\{^{1}H\}$ NMR spectrum of **14d** in C_6D_6.

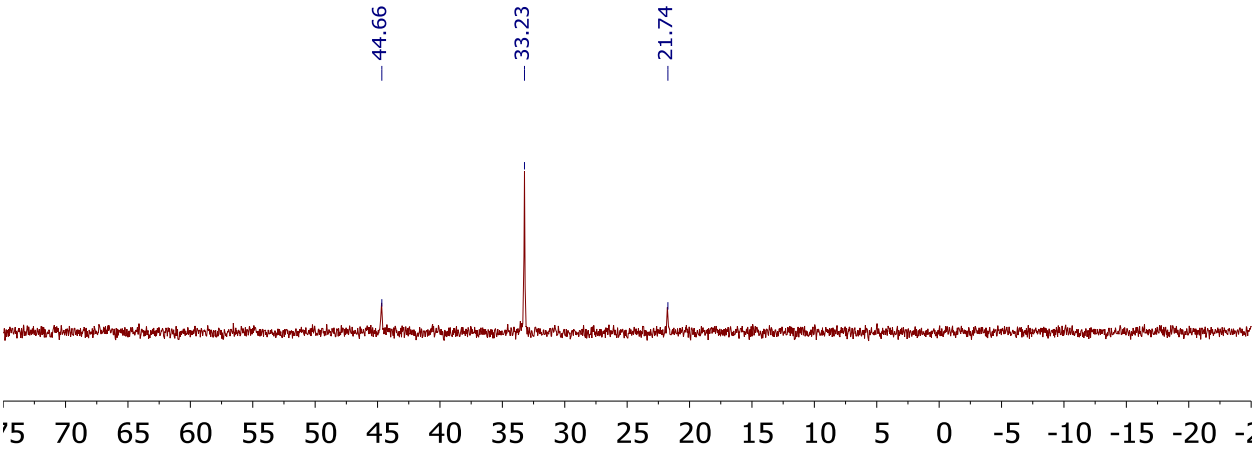


Figure S47. ^{1}H NMR spectrum of **15a** in C_6D_6.

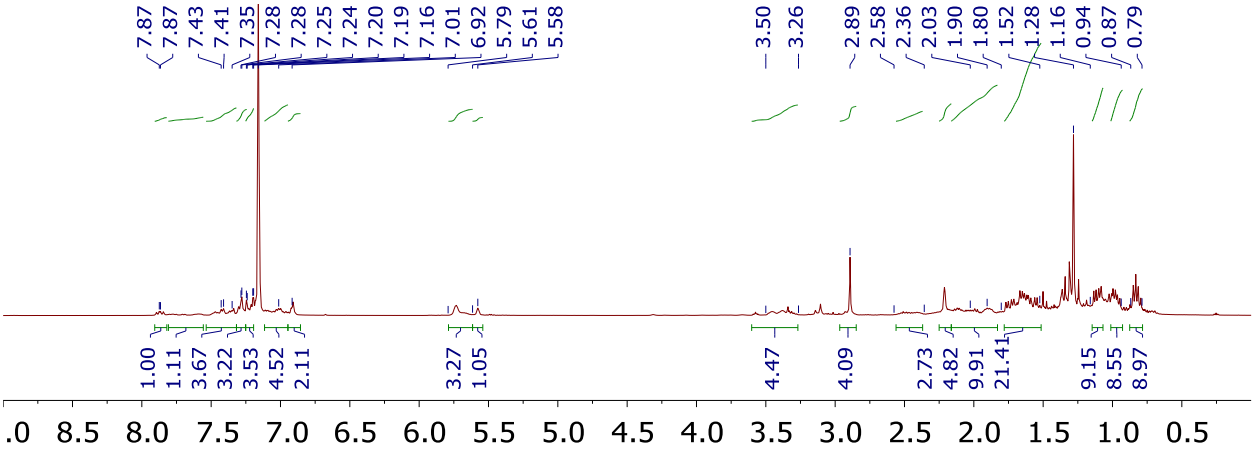


Figure S48. $^{13}C\{^{1}H\}$ NMR spectrum of **15a** in C_6D_6.

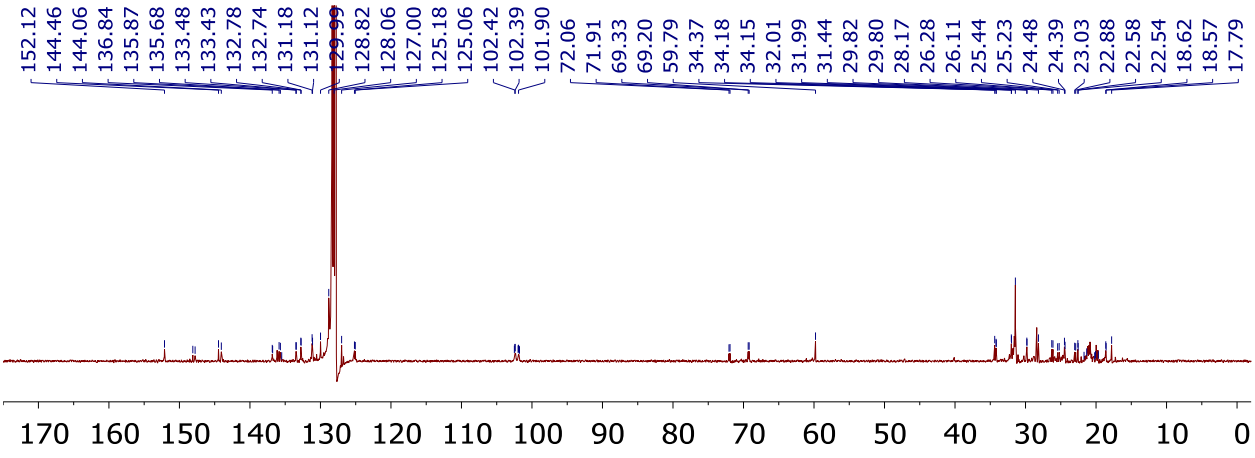


Figure S49. $^{31}P\{^{1}H\}$ NMR spectrum of **15a** in C_6D_6.

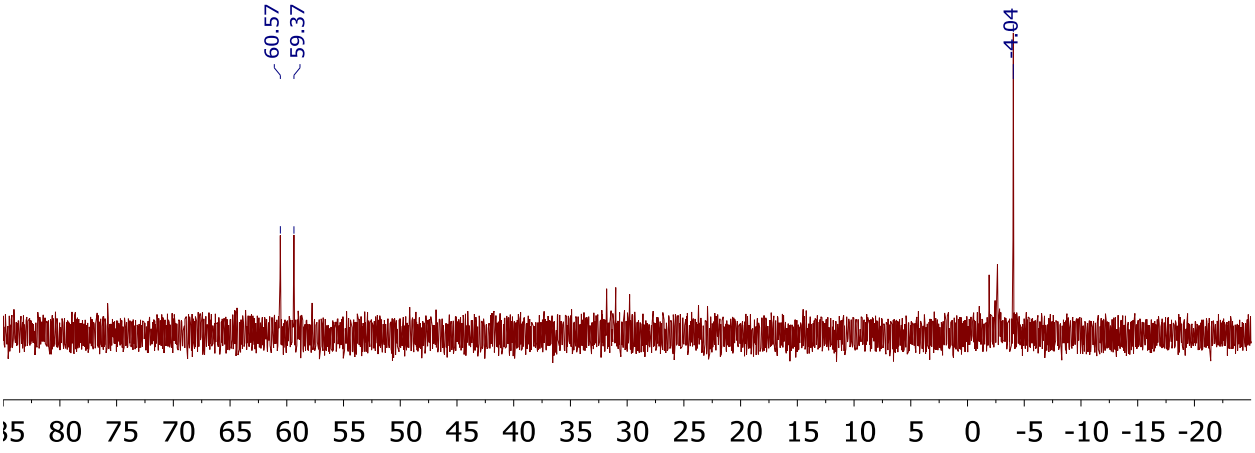


Figure S50. ^{1}H NMR spectrum of **19a** at 25 °C in C_6D_6.

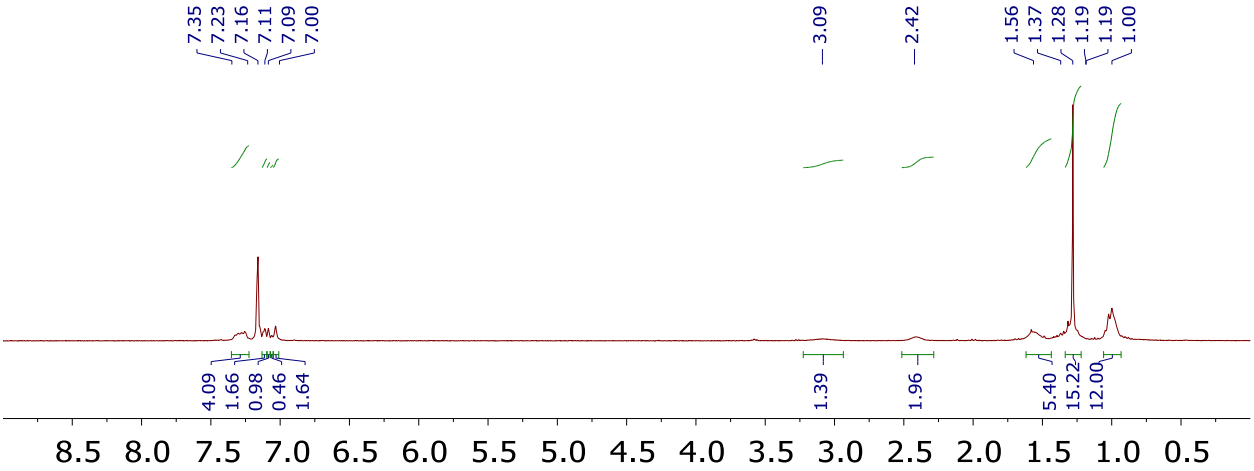


Figure S51. $^{31}P\{^{1}H\}$ NMR spectrum of **19a** at 25 °C in C_6D_6.

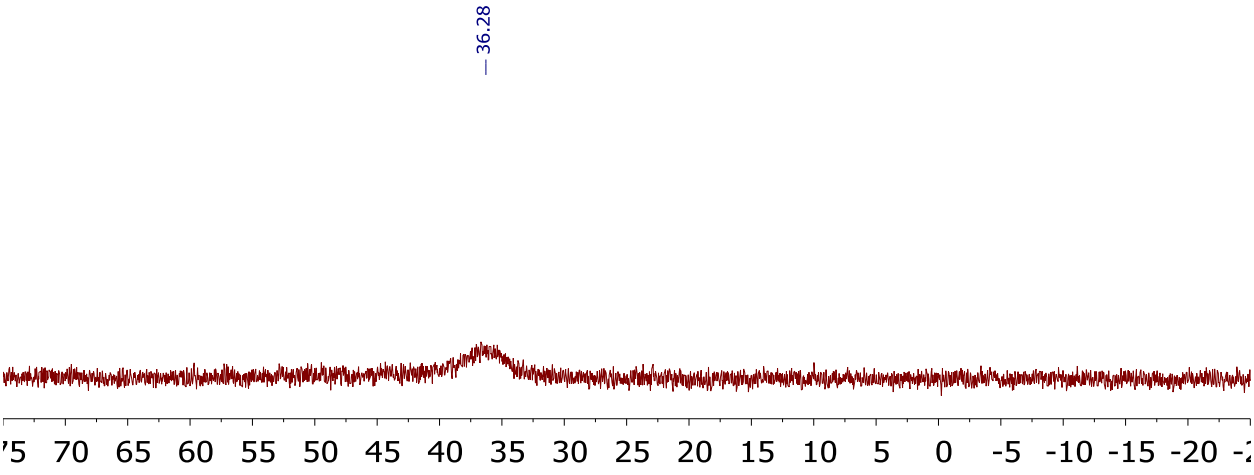


Figure S52. $^{13}C\{^{1}H\}$ NMR spectrum of **19a** at 70 °C in C_6D_6.

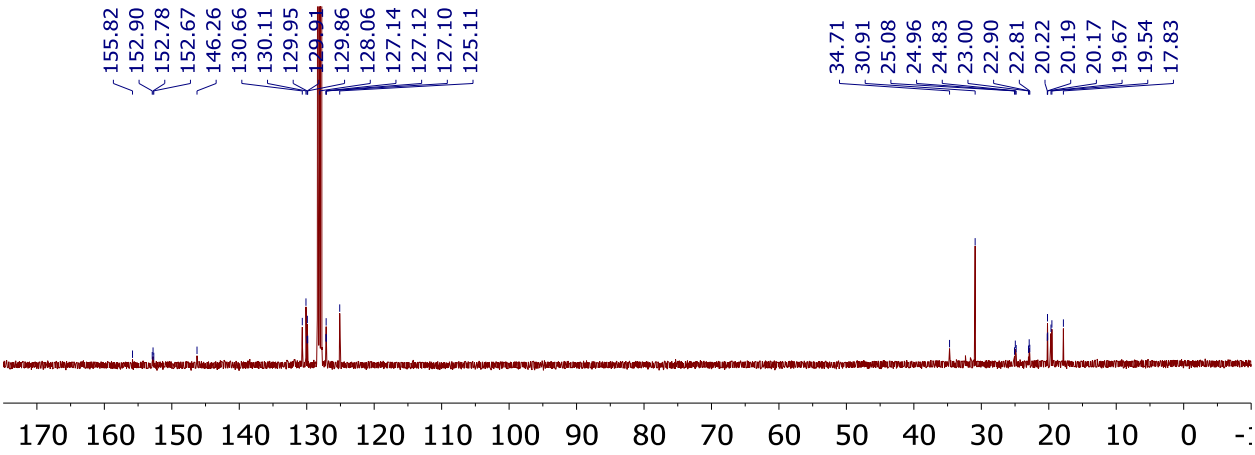


Figure S53. $^{31}P\{^{1}H\}$ NMR spectrum of **19a** at 70 °C in C_6D_6.

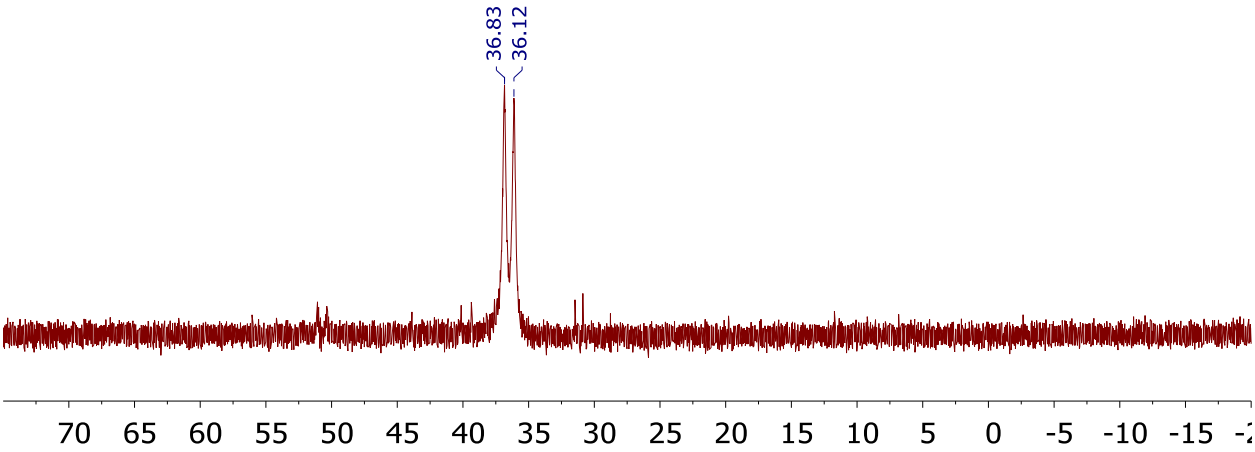


Figure S54. ^{1}H NMR spectrum of 1,3-bis(2'bromophenyl)-5-tert-butyl-benzene in $CDCl_3$. Note: Residual CH_3OH present.

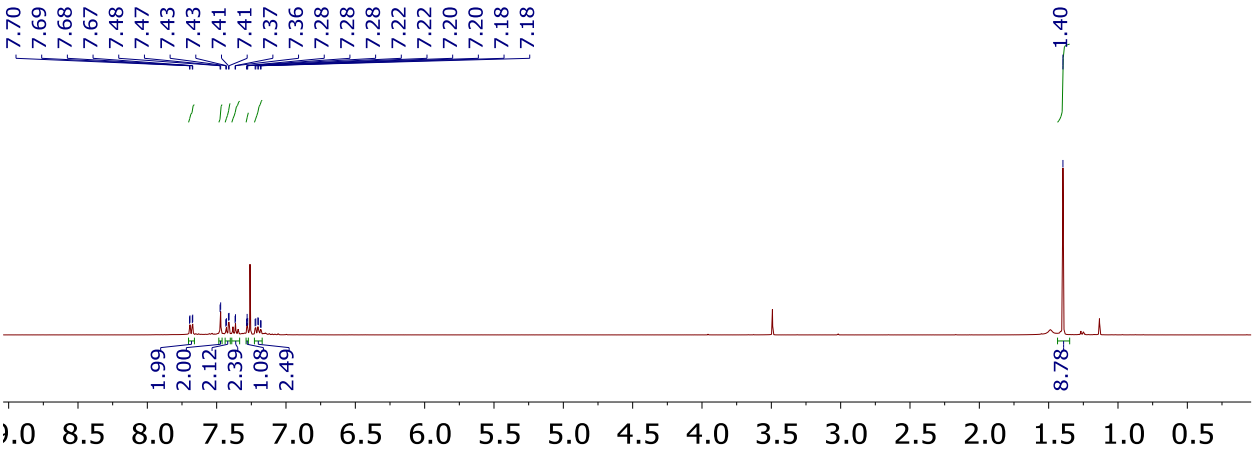


Figure S55. ^{1}H NMR spectrum of **1e** in C_6D_6.

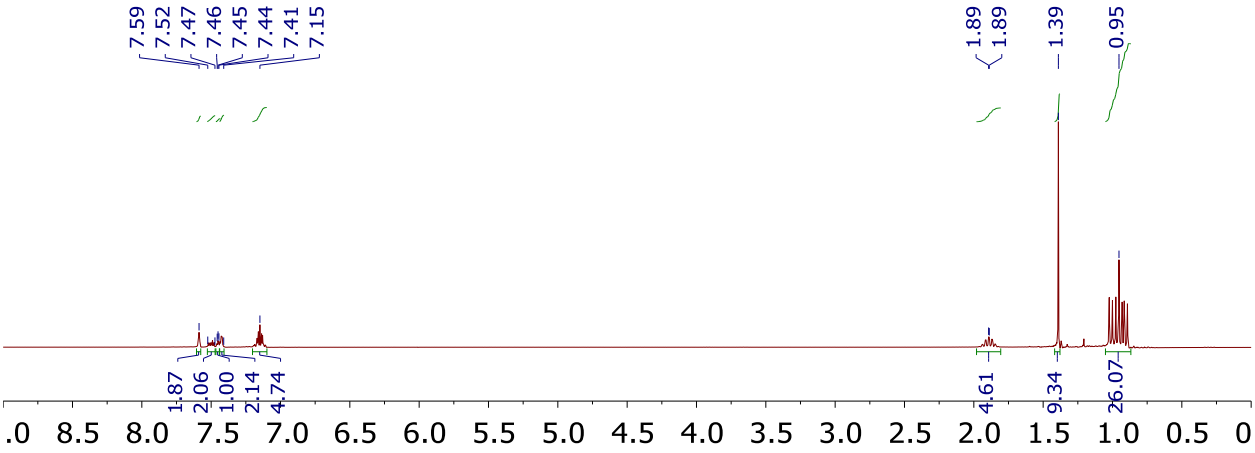


Figure S56. $^{13}C\{^{1}H\}$ NMR spectrum of **1e** in $CDCl_3$.

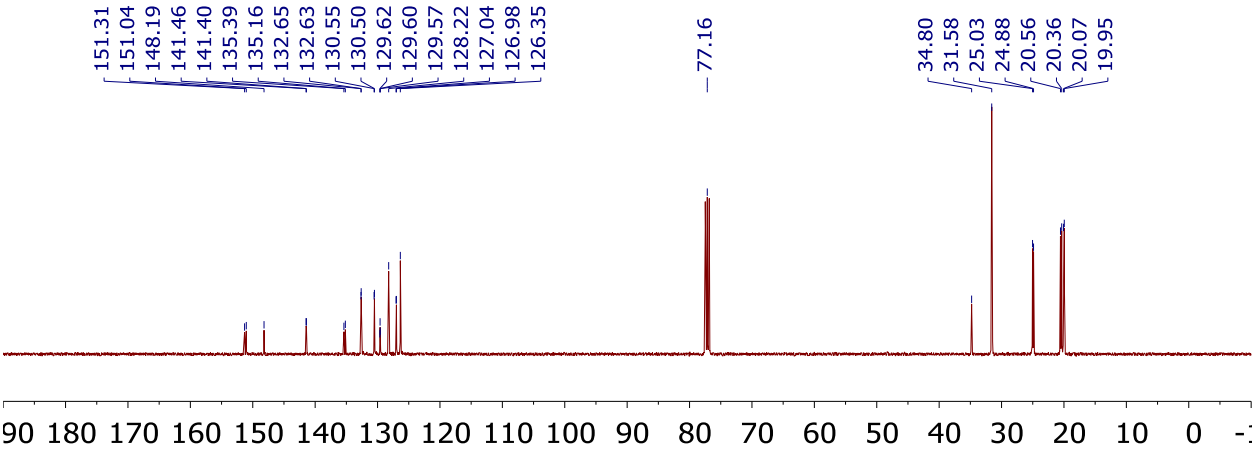


Figure S57. $^{31}P\{^{1}H\}$ NMR spectrum of **1e** in C_6D_6.

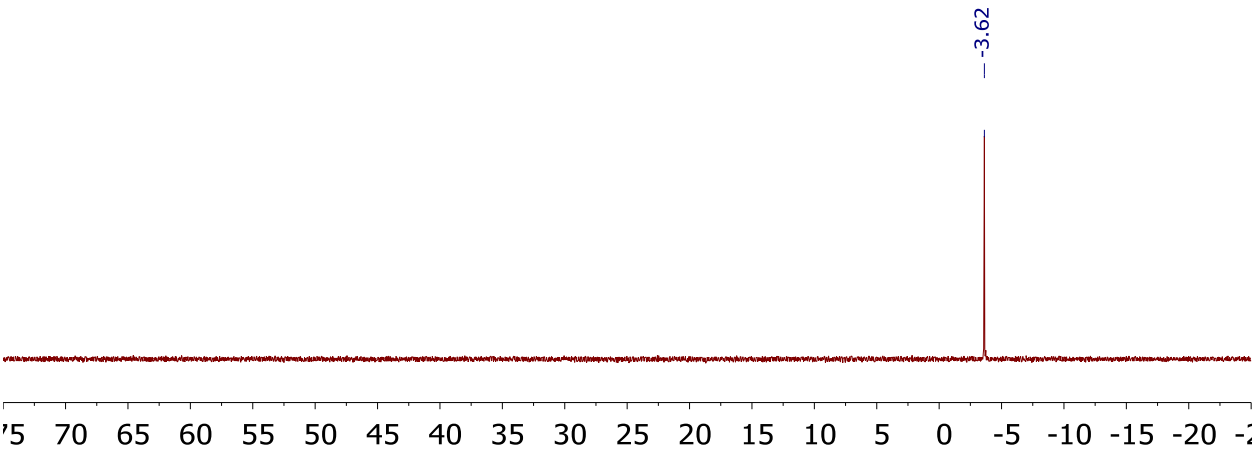


Figure S58. ^{1}H NMR spectrum of **23a** in C_6D_6.

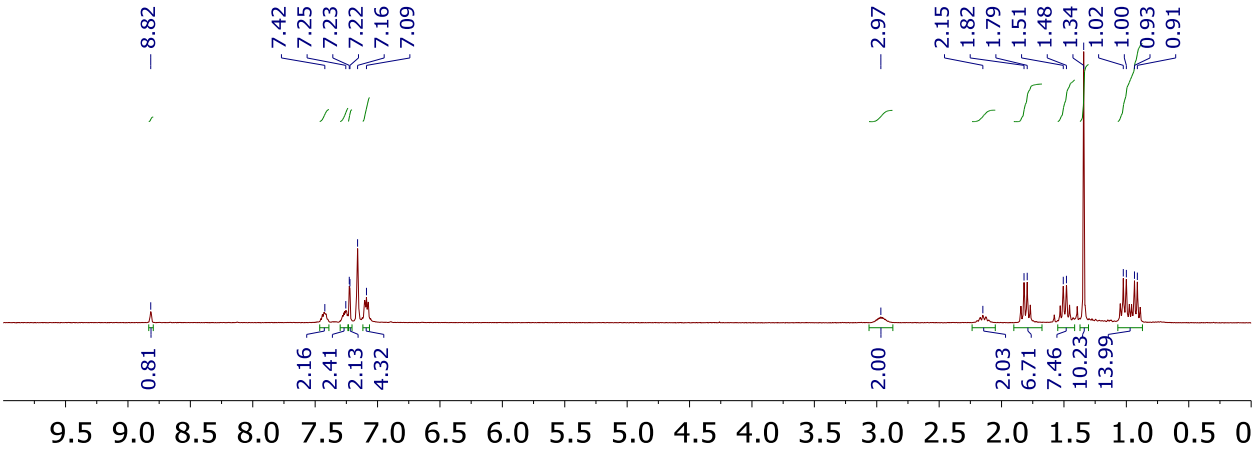


Figure S59. $^{13}C\{^{1}H\}$ NMR spectrum of **23a** in C_6D_6.

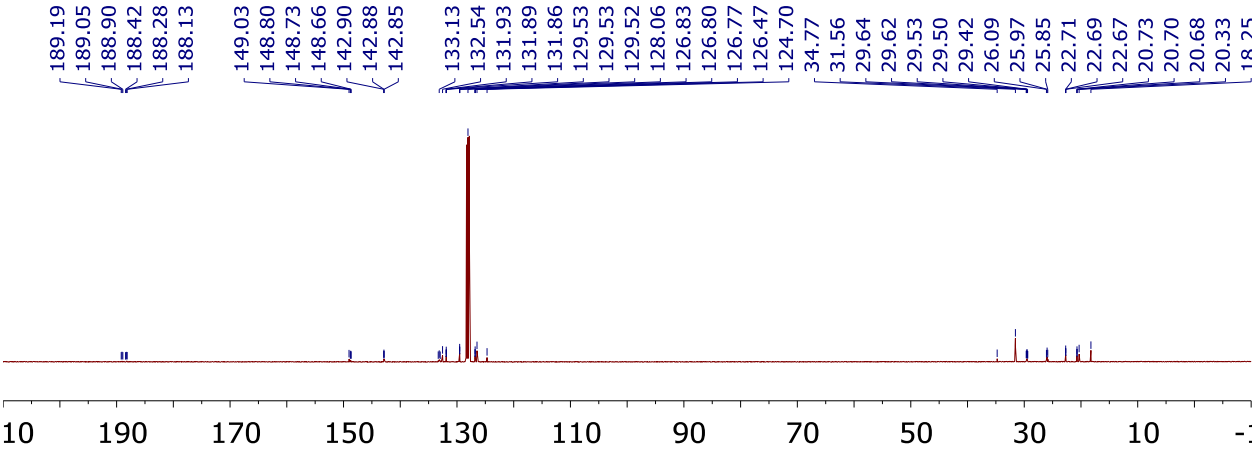


Figure S60. $^{31}P\{^{1}H\}$ NMR spectrum of **23a** in C_6D_6.

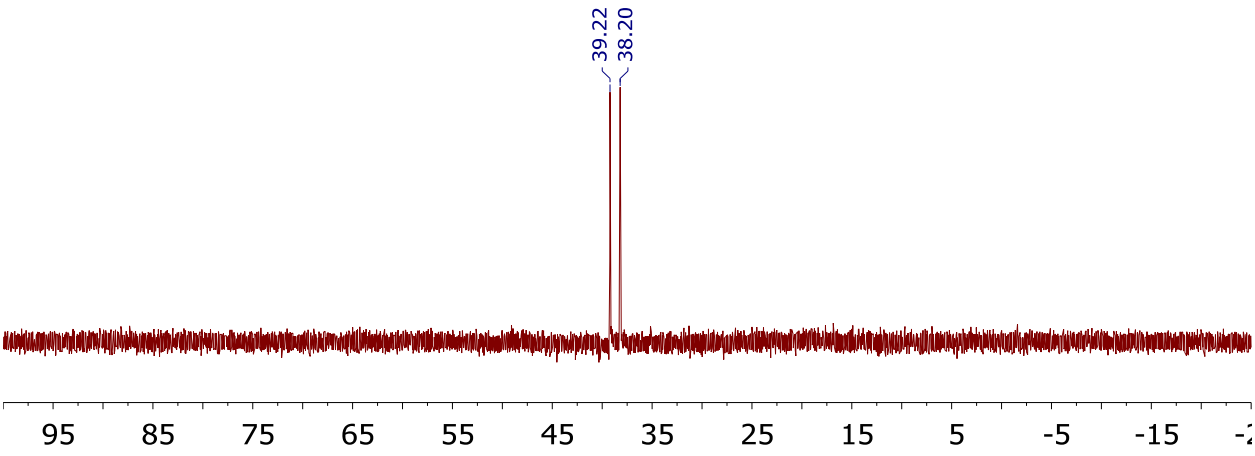


Figure S61. ^{1}H NMR spectrum of **24a** in C_6D_6.

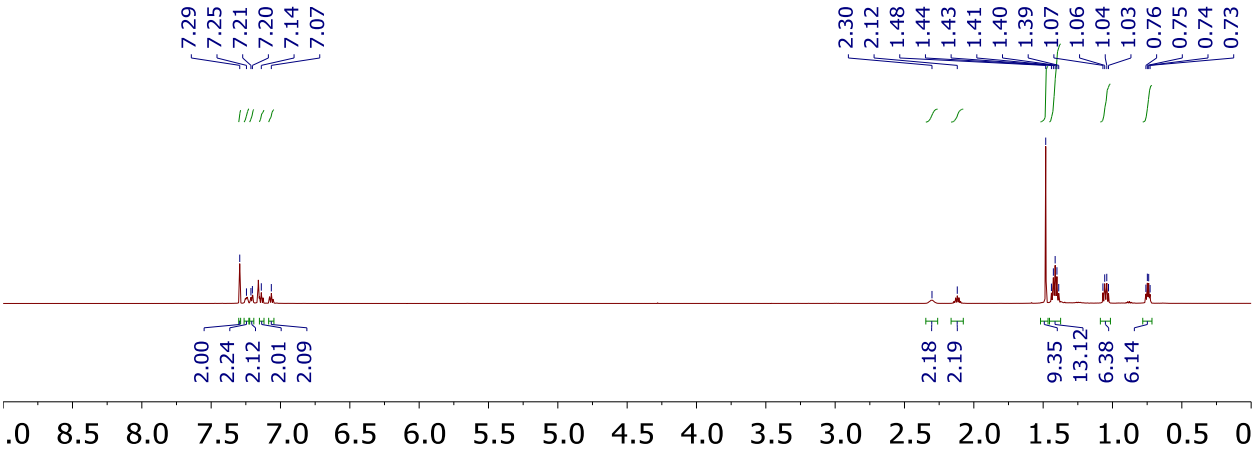


Figure S62. $^{13}C\{^{1}H\}$ NMR spectrum of **24a** in C_6D_6.

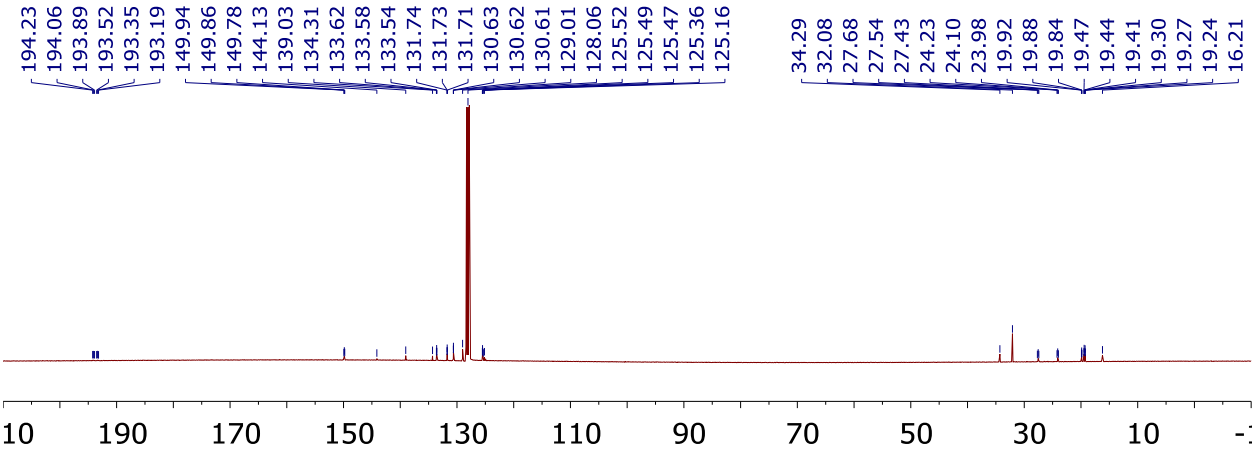


Figure S63. $^{31}P\{^{1}H\}$ NMR spectrum of **24a** in C_6D_6.

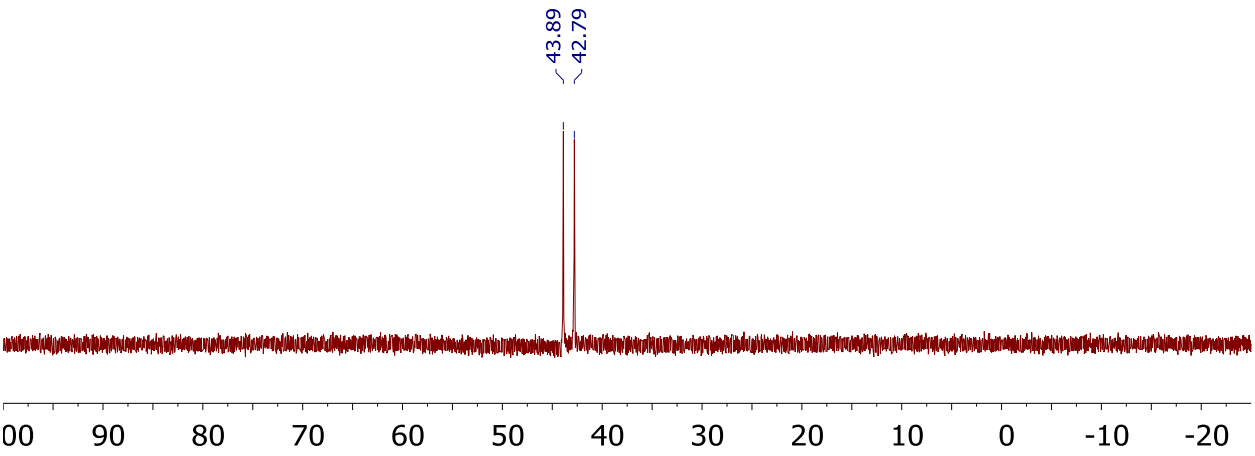


Figure S64. ^{1}H NMR spectrum of 5-(tert-butyl)-1,3-diiodo-2-(methoxymethoxy)benzene in $CDCl_3$.

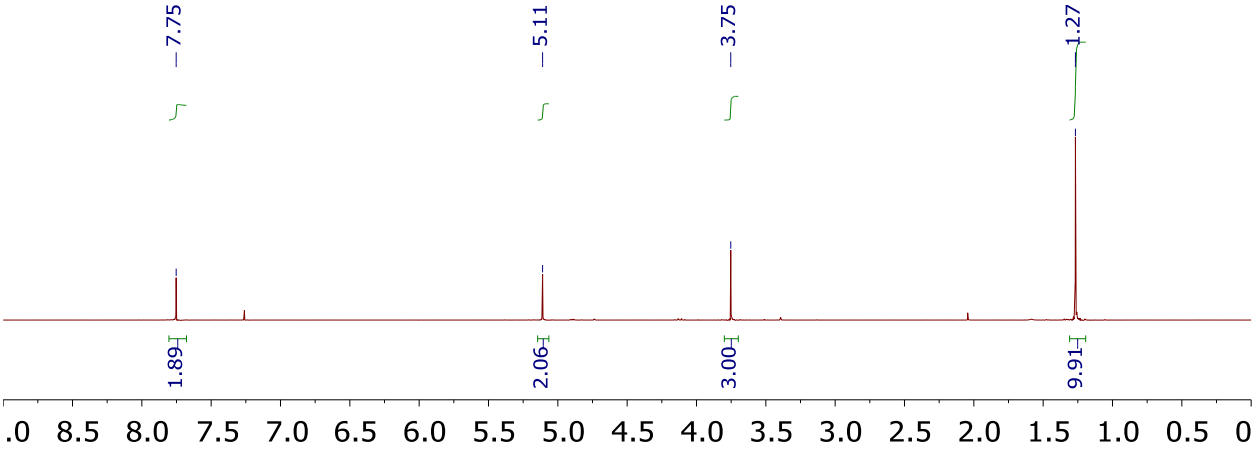


Figure S65. $^{13}C\{^{1}H\}$ NMR spectrum of 5-(tert-butyl)-1,3-diiodo-2-(methoxymethoxy)benzene in $CDCl_3$.

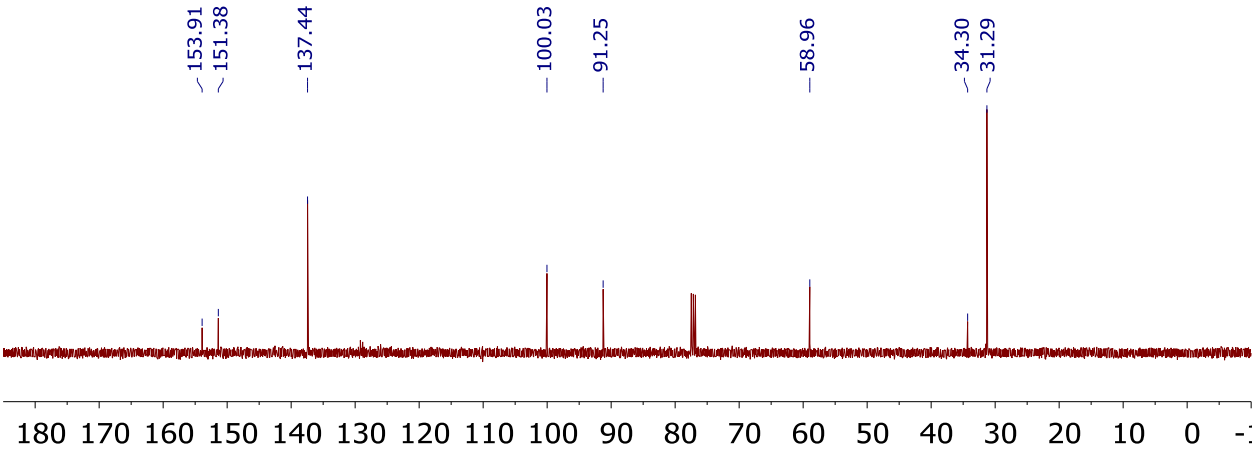


Figure S66. ^{1}H NMR spectrum of 1,3-bis(2'-bromophenyl)-5-tert-butyl-2-(methoxymethoxy)benzene in $CDCl_3$.

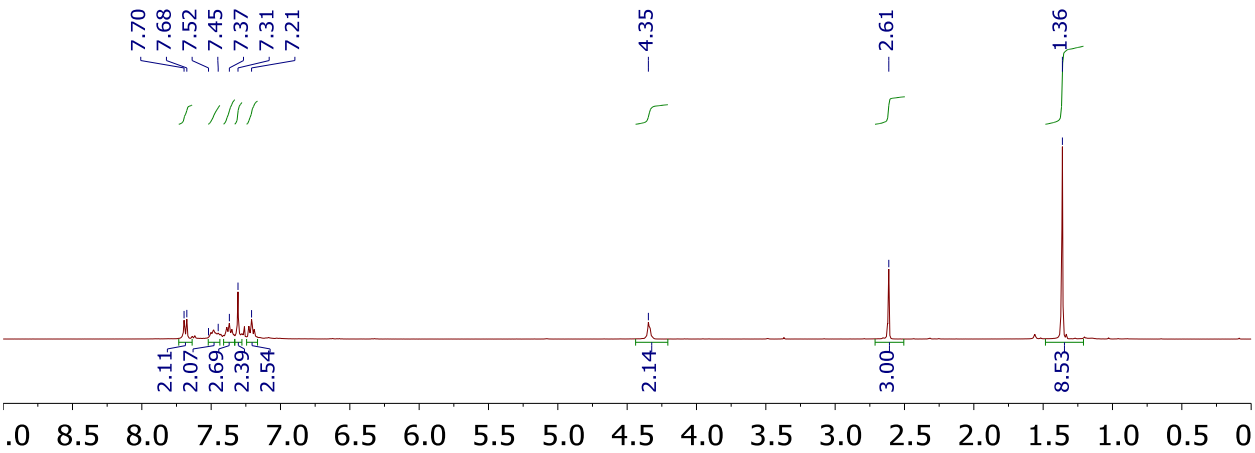


Figure S67. ^{1}H NMR spectrum of **1f** at 25 °C in C_6D_6.

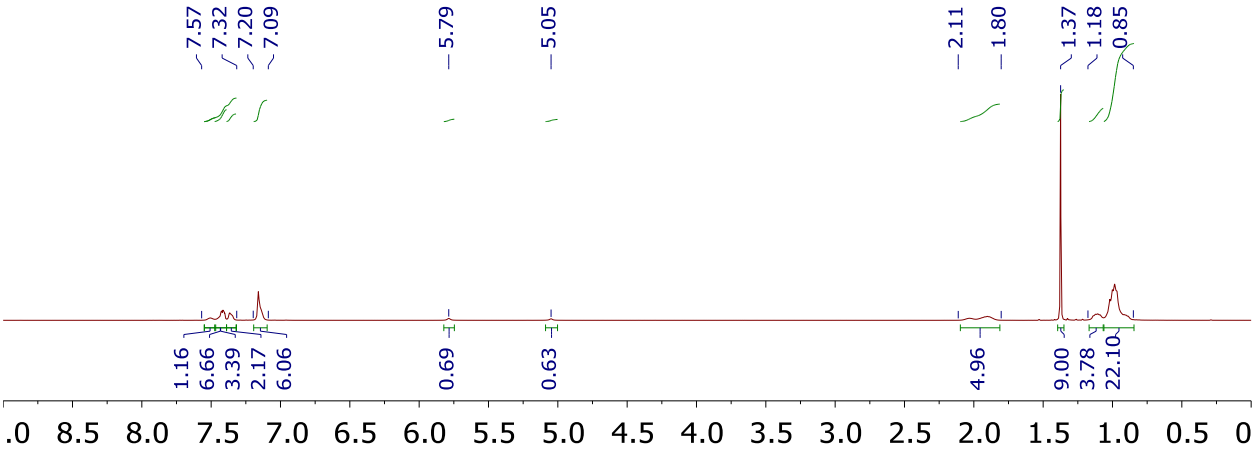


Figure S68. $^{31}P\{^{1}H\}$ NMR spectrum of **1f** at 25 °C in C_6D_6. Note: Referenced to solvent residual.

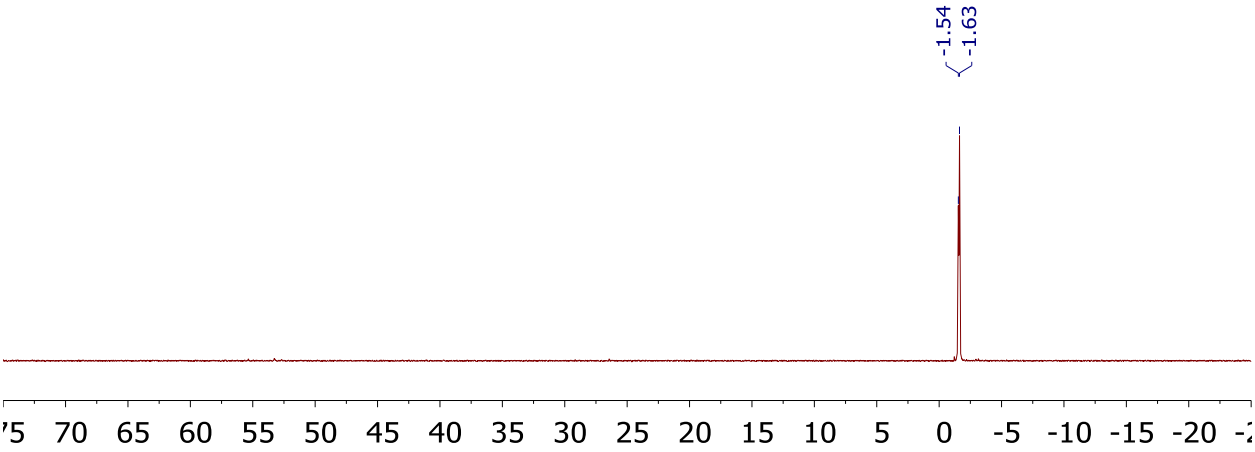


Figure S69. ^{1}H NMR spectrum of **1f** at 70 °C.

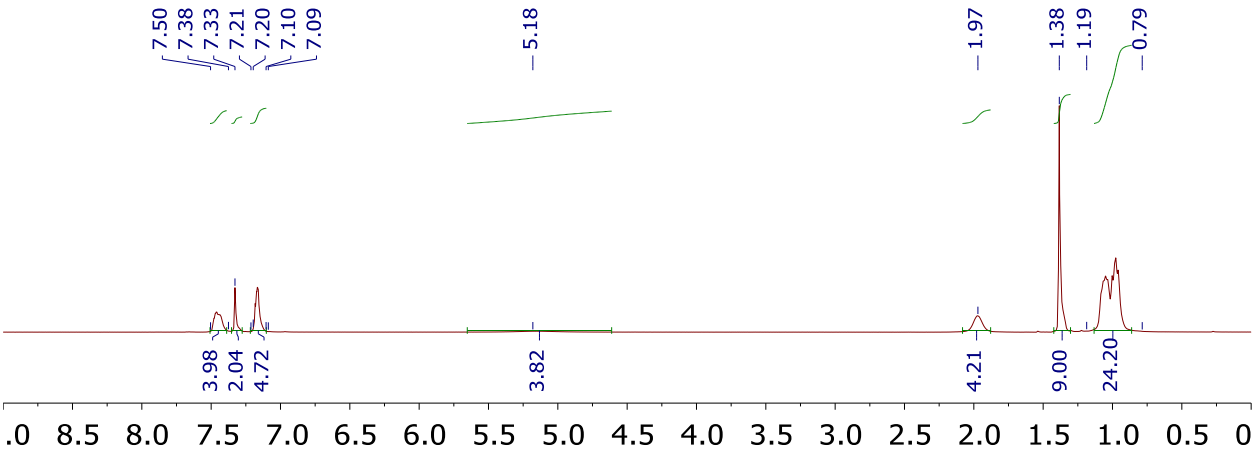


Figure S70. $^{13}C\{^{1}H\}$ NMR spectrum of **1f** at 70 °C in C_6D_6.

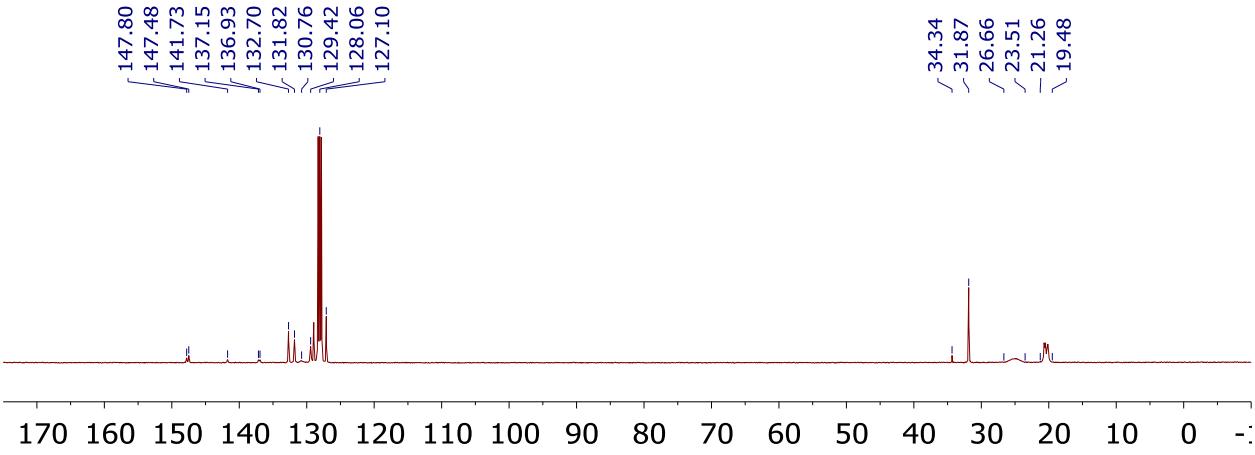


Figure S71. $^{31}P\{^{1}H\}$ NMR spectrum of **1f** at 70 °C in C_6D_6. Note: Referenced to solvent residual.

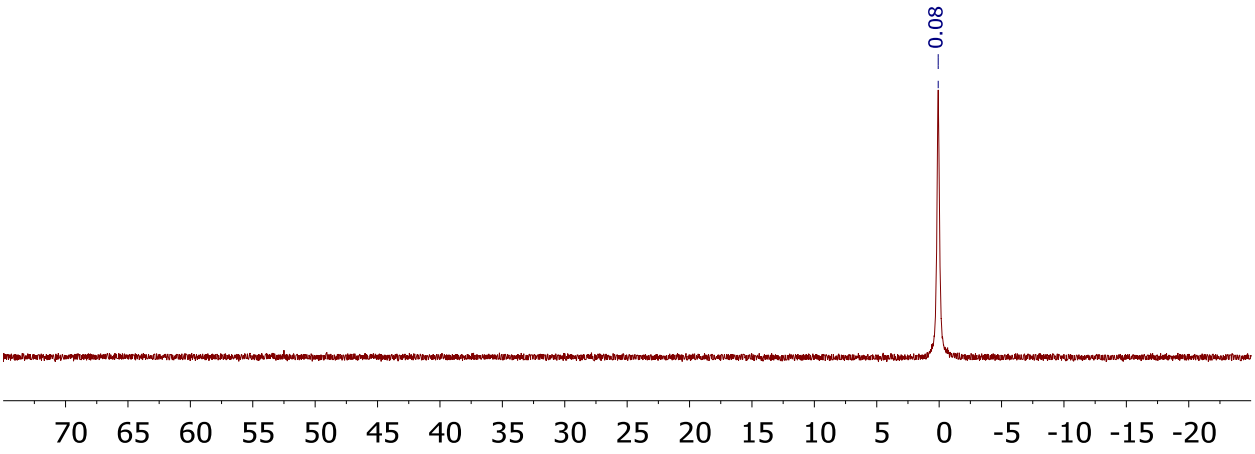


Figure S72. ^{1}H NMR spectrum of **26a** in C_6D_6.

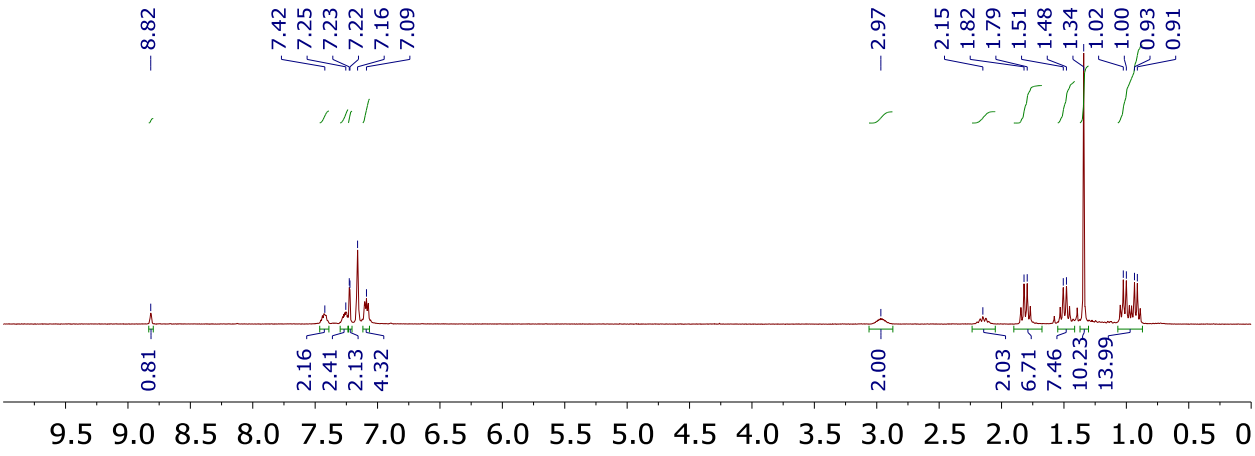


Figure S73. $^{13}C\{^{1}H\}$ NMR spectrum of **26a** in C_6D_6.

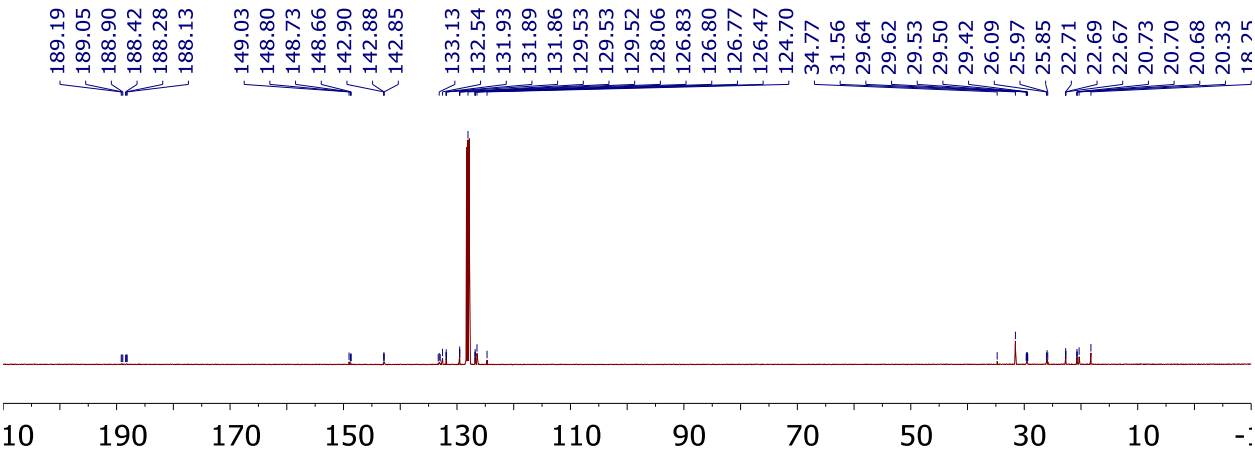


Figure S74. $^{31}P\{^{1}H\}$ NMR spectrum of **26a** in C_6D_6.

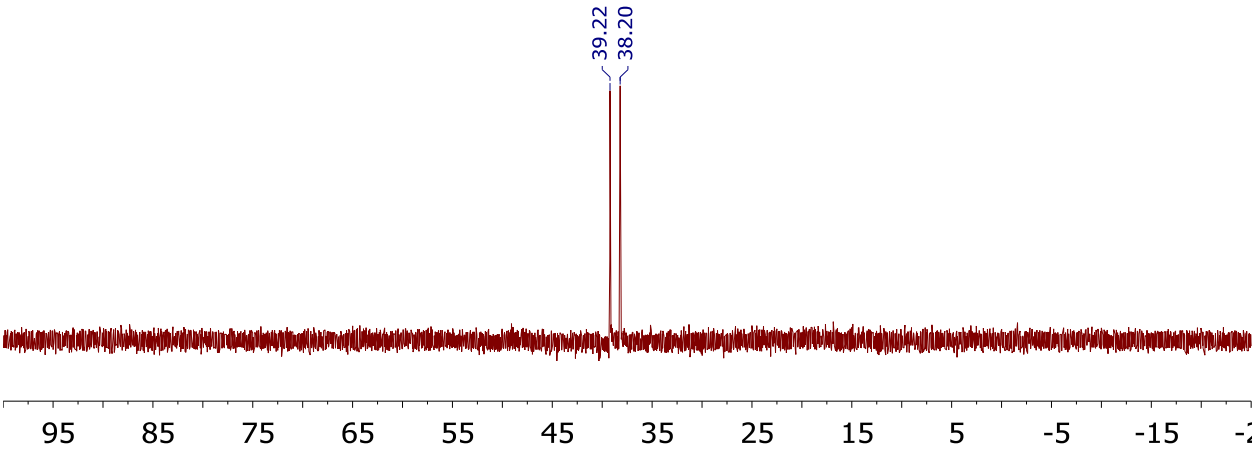


Figure S75. ^{1}H NMR spectrum of **27a** in C_6D_6.

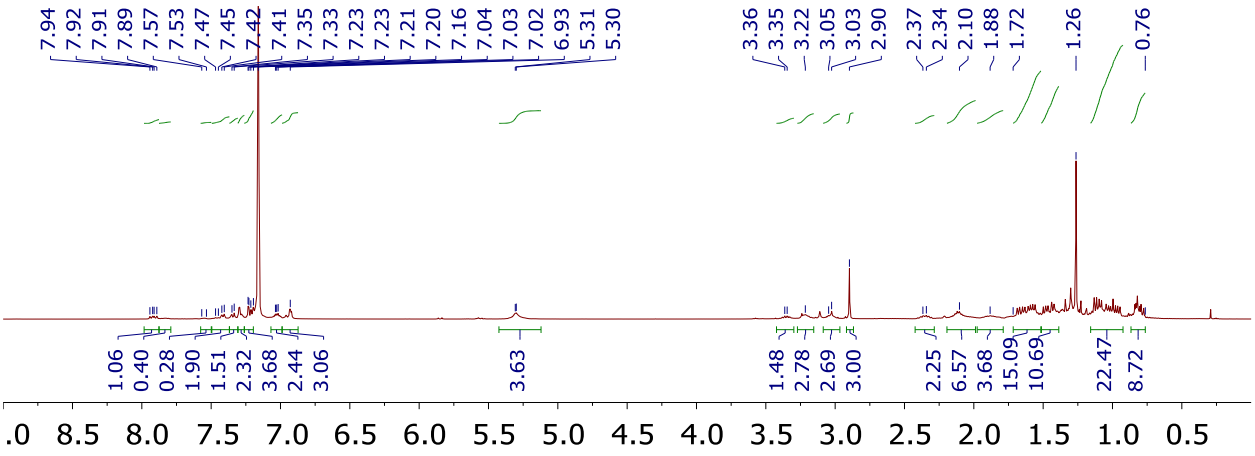


Figure S76. $^{13}C\{^{1}H\}$ NMR spectrum of **27a** in C_6D_6.

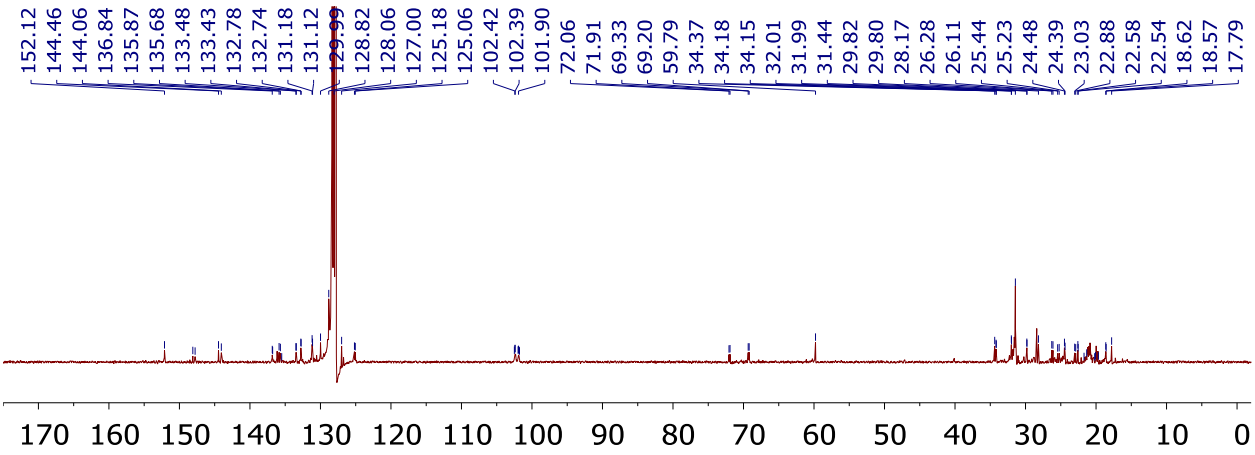


Figure S77. $^{31}P\{^{1}H\}$ NMR spectrum of **27a** in C_6D_6.

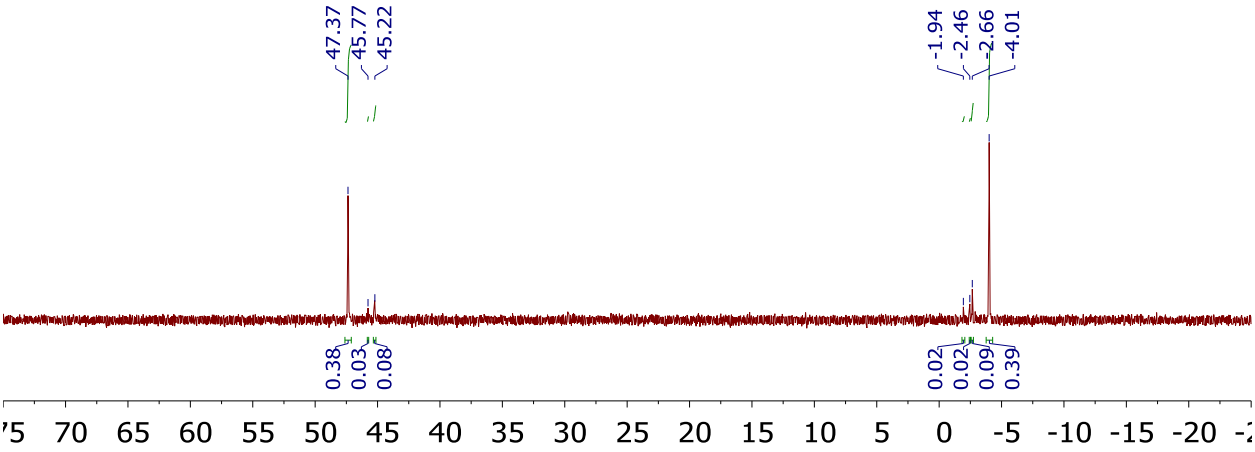


Figure S78. ^{1}H NMR spectrum of **28a** in C_6D_6.

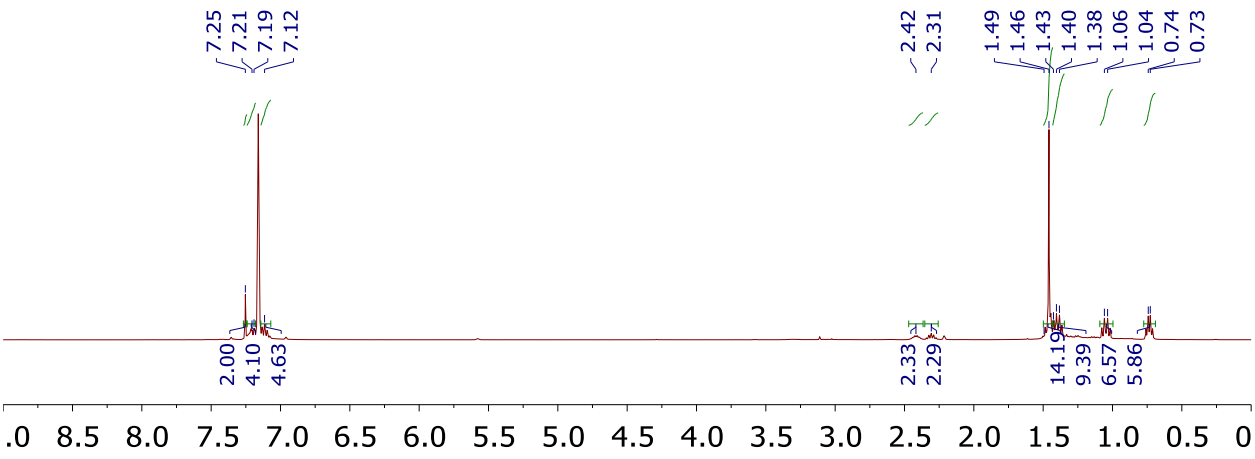


Figure S79. $^{13}C\{^{1}H\}$ NMR spectrum of **28a** in C_6D_6.

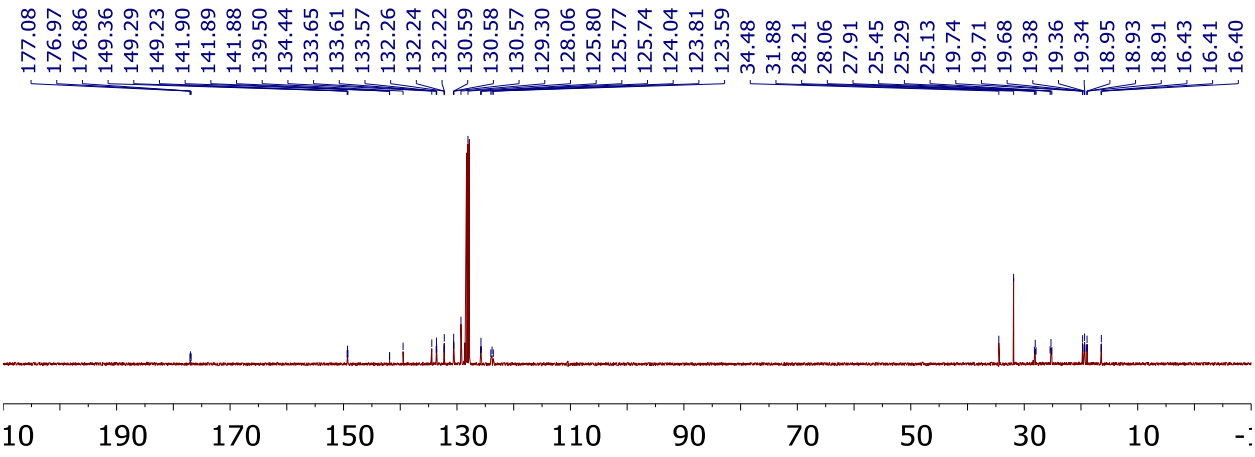


Figure S80. $^{31}P\{^{1}H\}$ NMR spectrum of **28a** in C_6D_6.

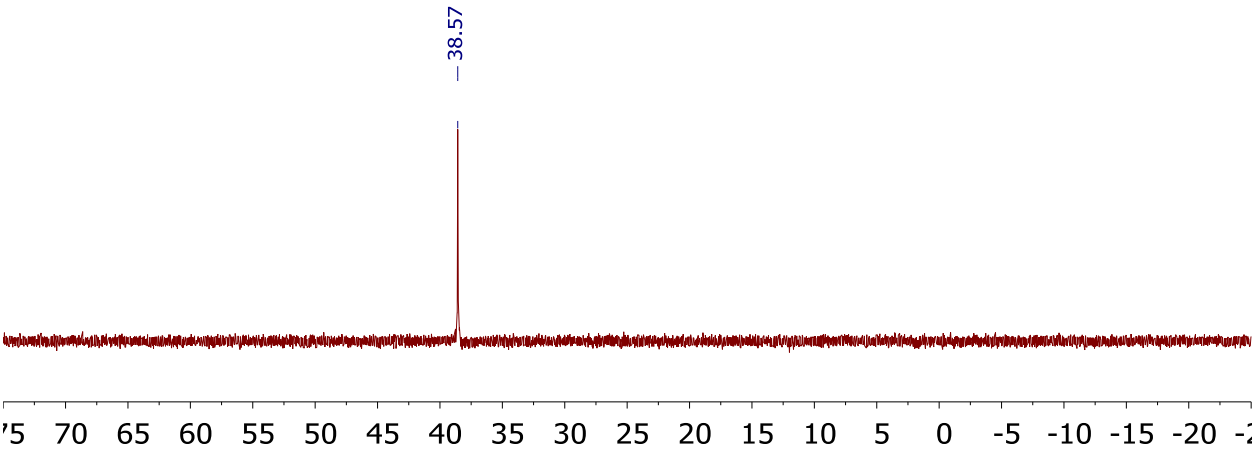


Figure S81. ^{1}H NMR spectrum of **29a** in C_6D_6. Note: Residual 1,5-cyclooctadiene present.

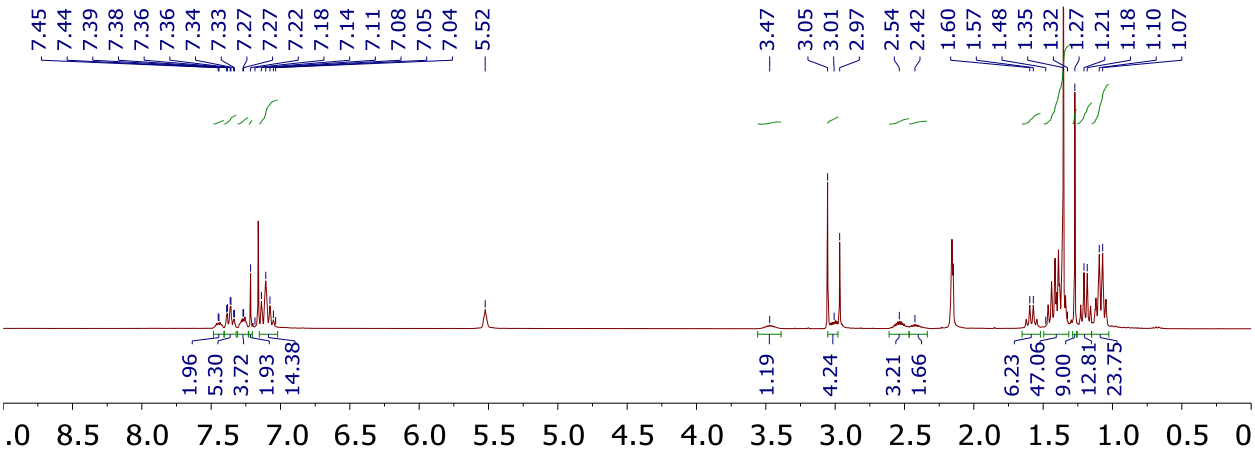


Figure S82. $^{13}C\{^{1}H\}$ NMR spectrum of **29a** in C_6D_6. Note: Residual 1,5-cyclooctadiene present.

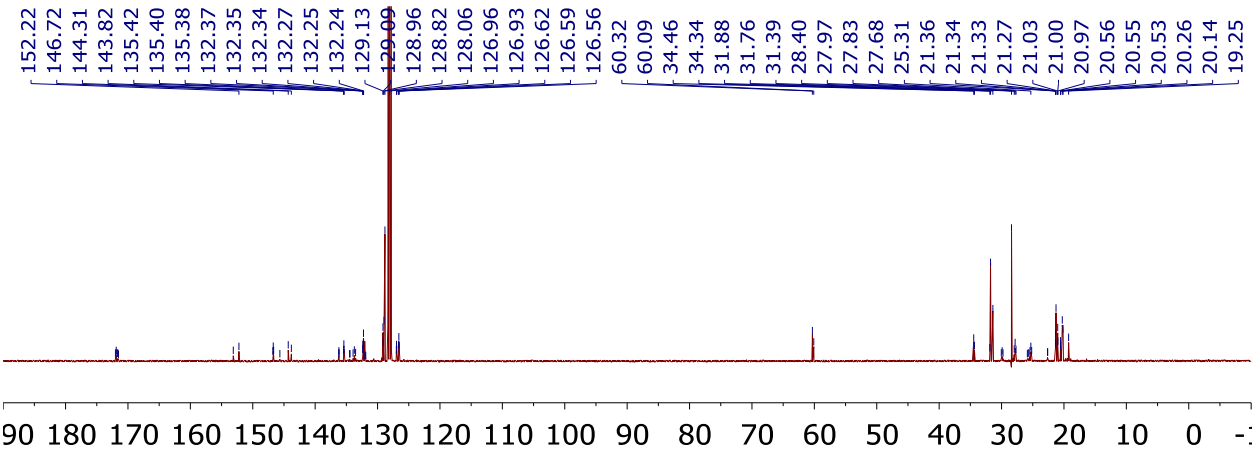


Figure S83. $^{31}P\{^{1}H\}$ NMR spectrum of **29a** in C_6D_6.

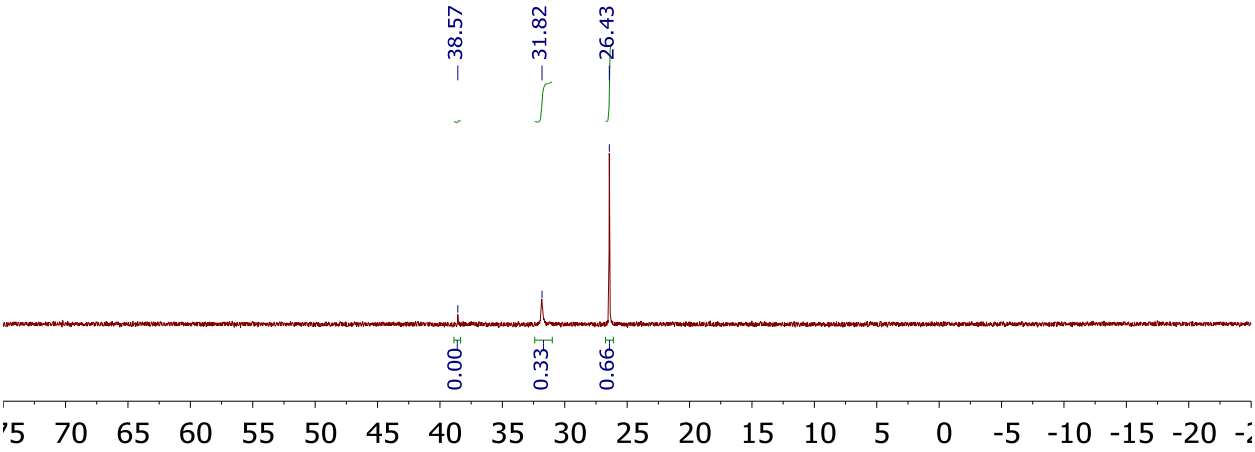


Figure S84. ^{1}H NMR spectrum of **32a** in C_6D_6. Note: Residual toluene present.

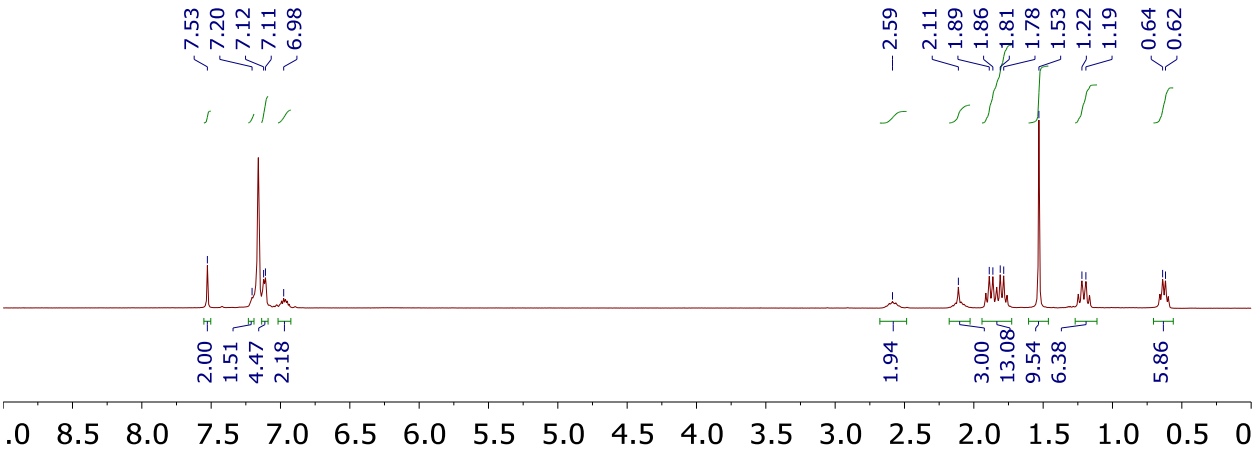


Figure S85. $^{13}C\{^{1}H\}$ NMR spectrum of **32a** in C_6D_6. Note: Residual toluene present.

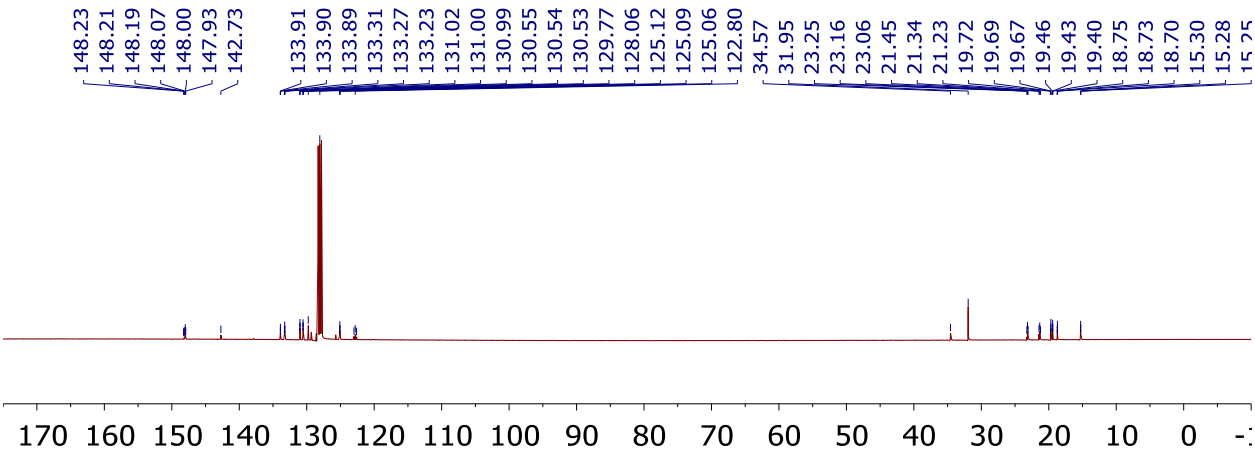


Figure S86. $^{31}P\{^{1}H\}$ NMR spectrum of **32a** in C_6D_6.

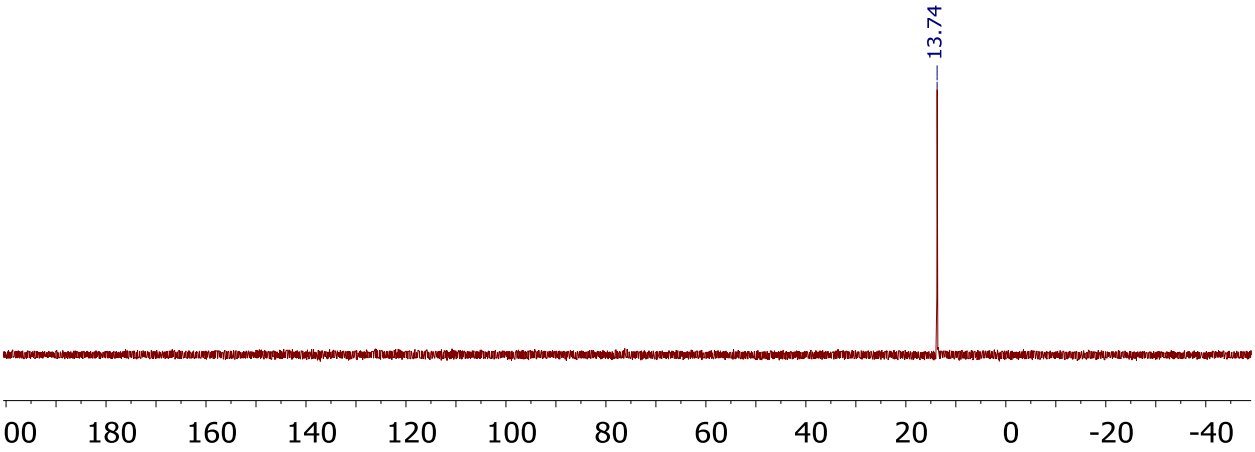


Figure S87. ^{1}H NMR spectrum of **32b** in C_6D_6.

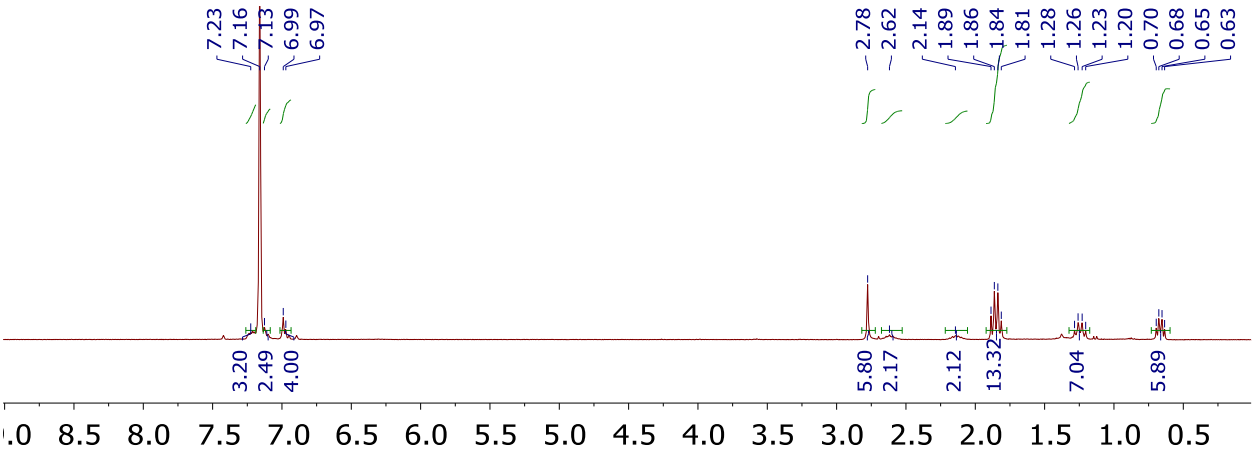


Figure S88. $^{13}C\{^{1}H\}$ NMR spectrum of **32b** in C_6D_6.

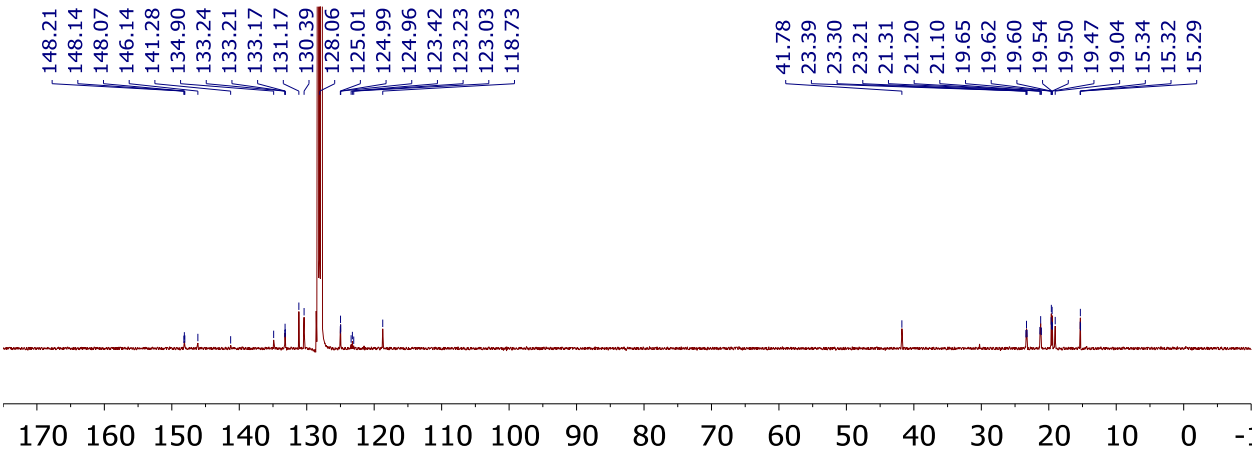


Figure S89. $^{31}P\{^{1}H\}$ NMR spectrum of **32b** in C_6D_6.

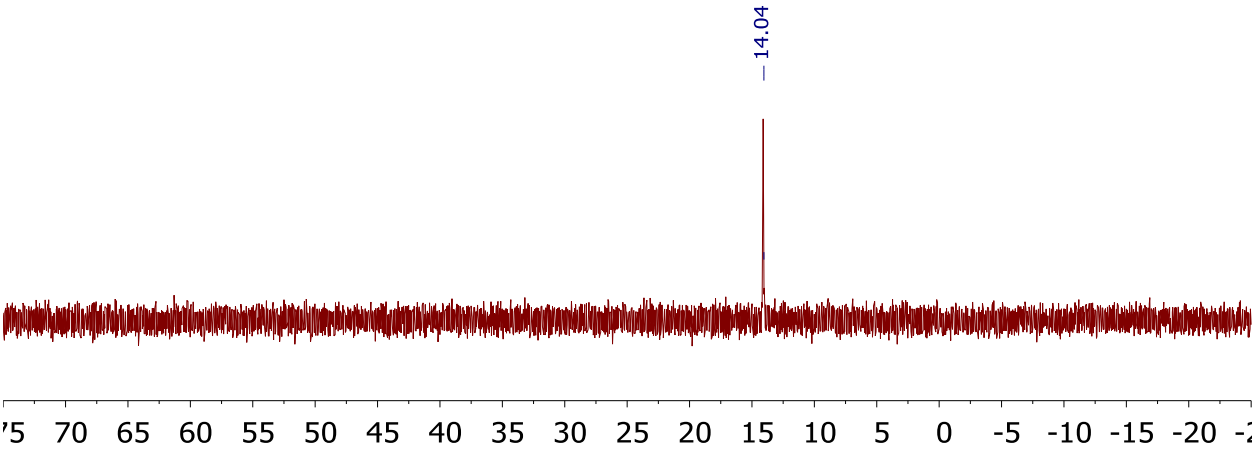


Figure S90. ^{1}H NMR spectrum of **33a** in C_6D_6.

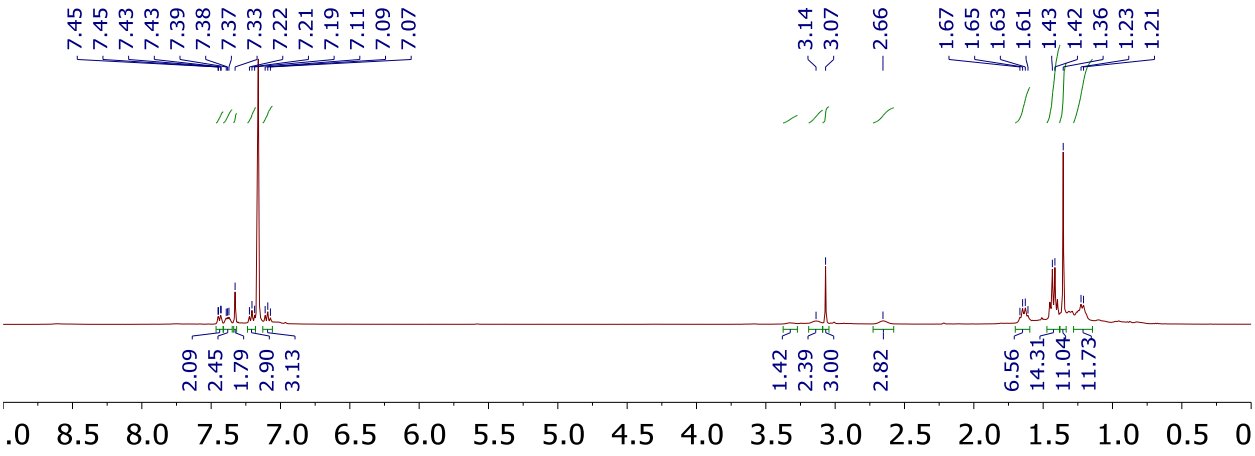


Figure S91. $^{13}C\{^{1}H\}$ NMR spectrum of **33a** in C_6D_6.

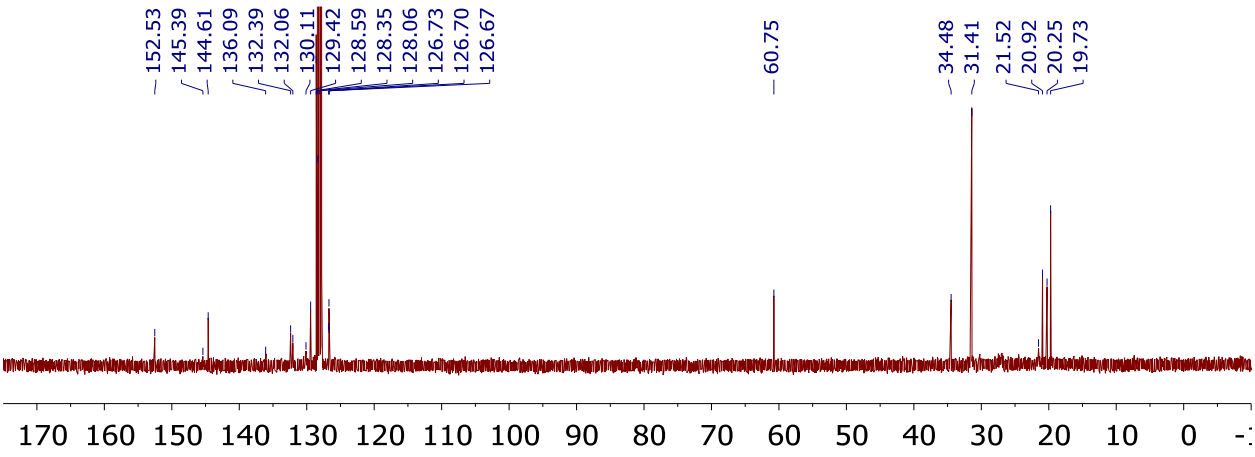


Figure S92. $^{31}P\{^{1}H\}$ NMR spectrum of **33a** in C_6D_6.

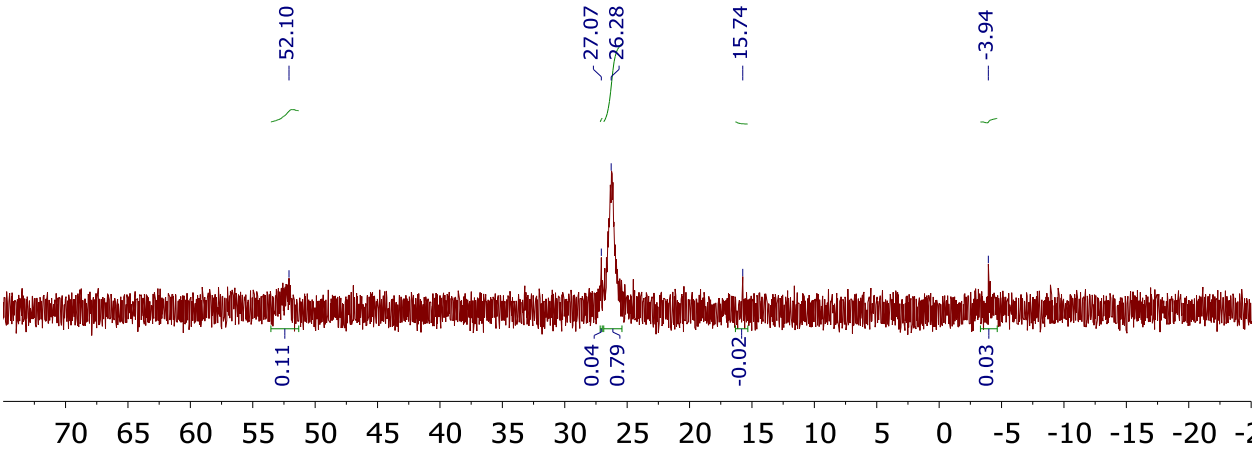


Figure S93. ^{1}H NMR spectrum of **34a** in CD_3CN.

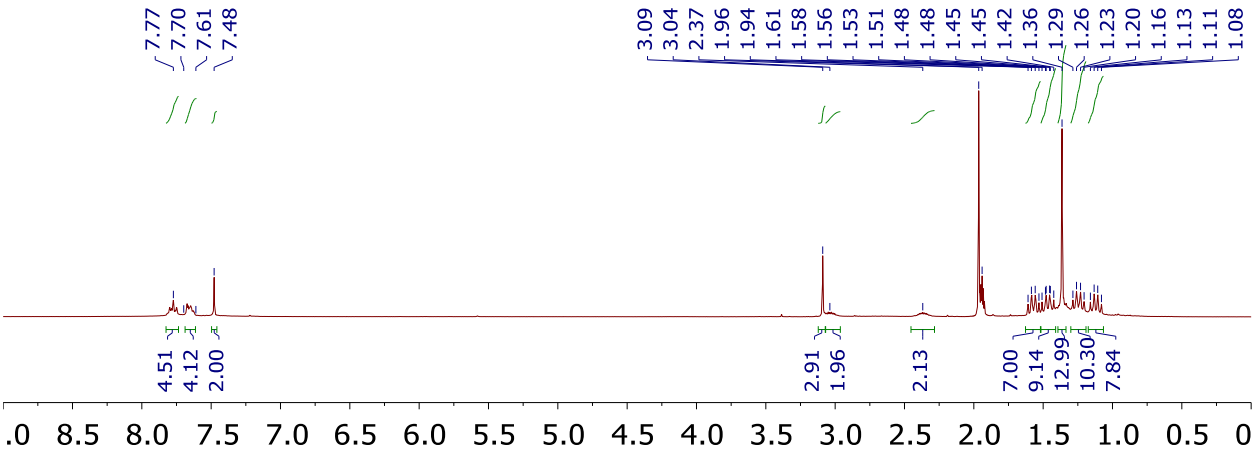


Figure S94. $^{13}C\{^{1}H\}$ NMR spectrum of **34a** in CD_3CN.

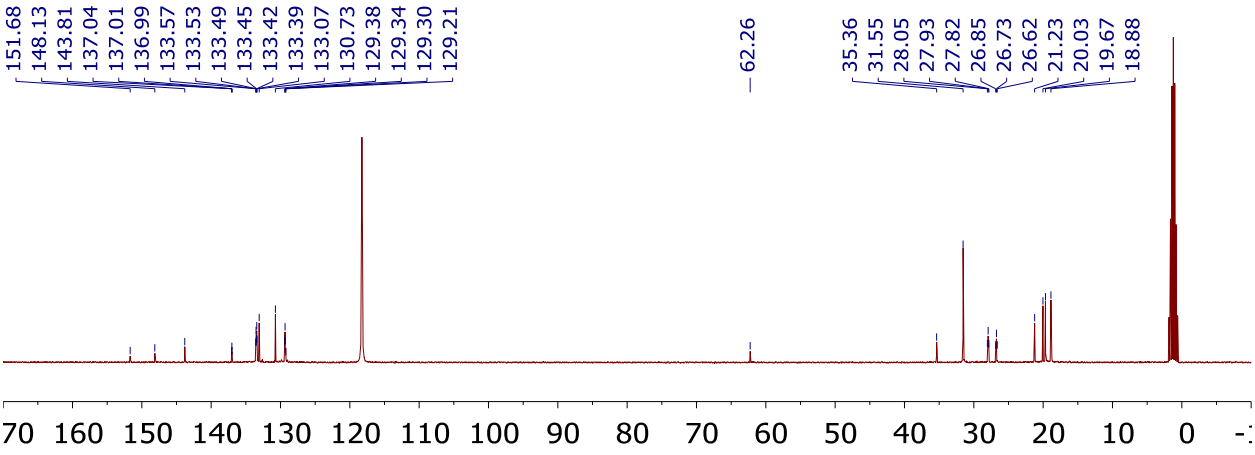


Figure S95. ^{19}F NMR spectrum of **34a** in CD_3CN.

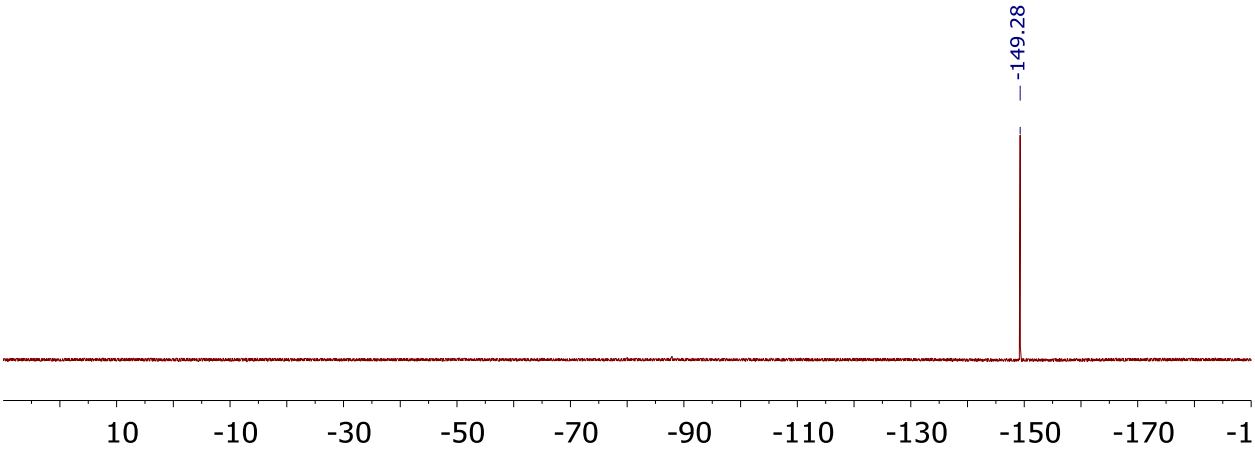


Figure S96. $^{31}P\{^{1}H\}$ NMR spectrum of **34a** in CD_3CN.

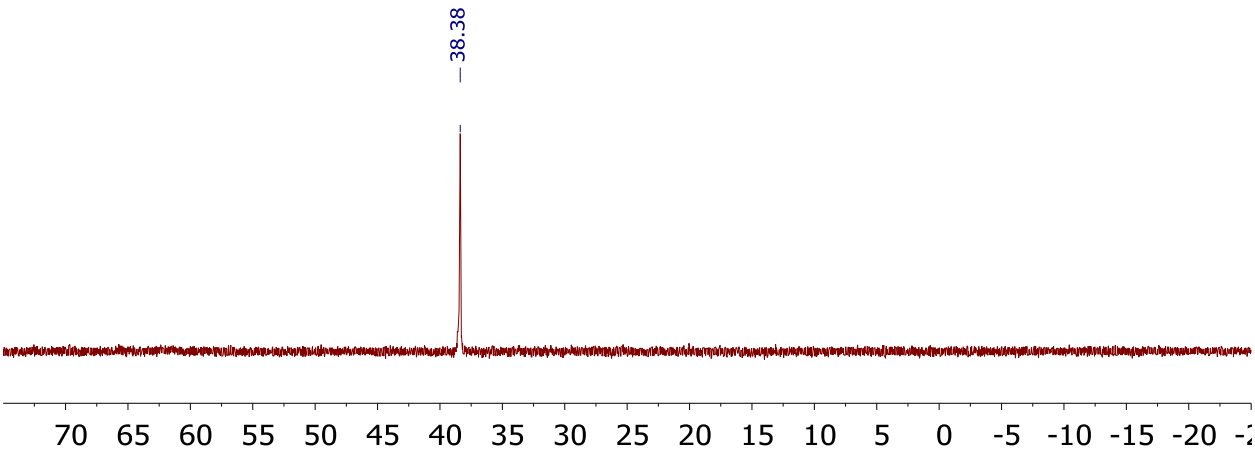


Figure S97. ^{1}H NMR spectrum of **35a** in C_6D_6.

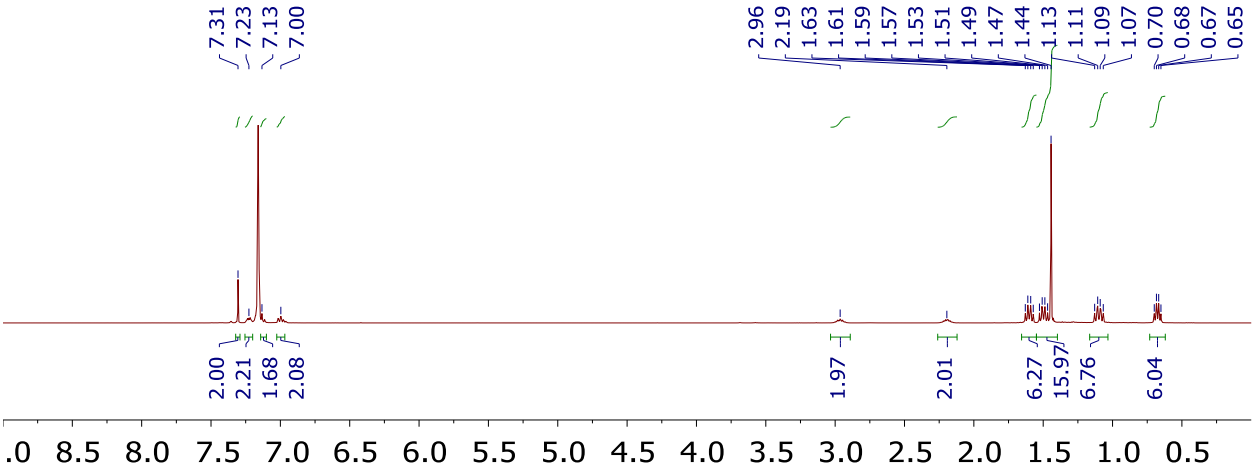


Figure S98. $^{13}C\{^{1}H\}$ NMR spectrum of **35a** in C_6D_6.

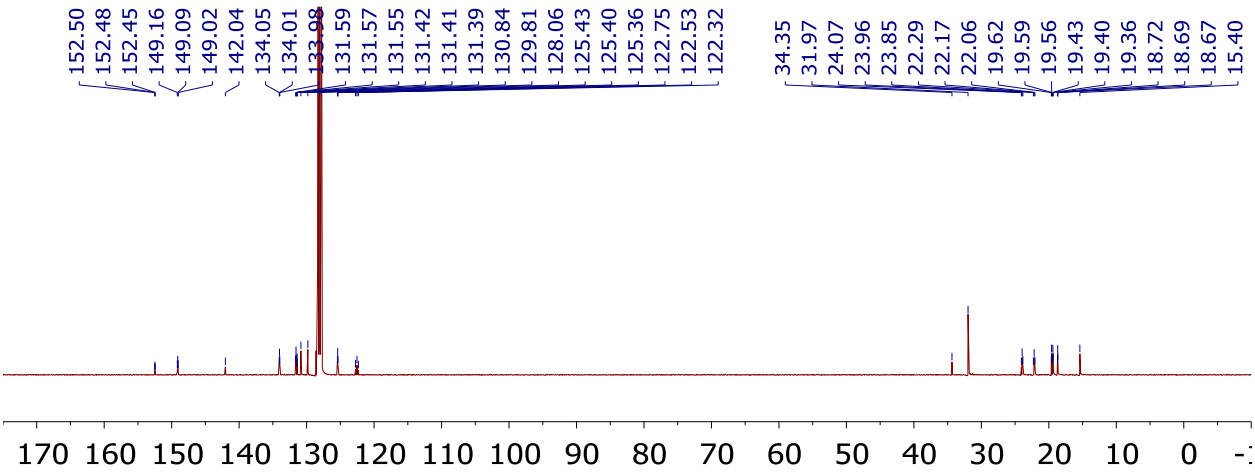


Figure S99. $^{31}P\{^{1}H\}$ NMR spectrum of **35a** in C_6D_6.

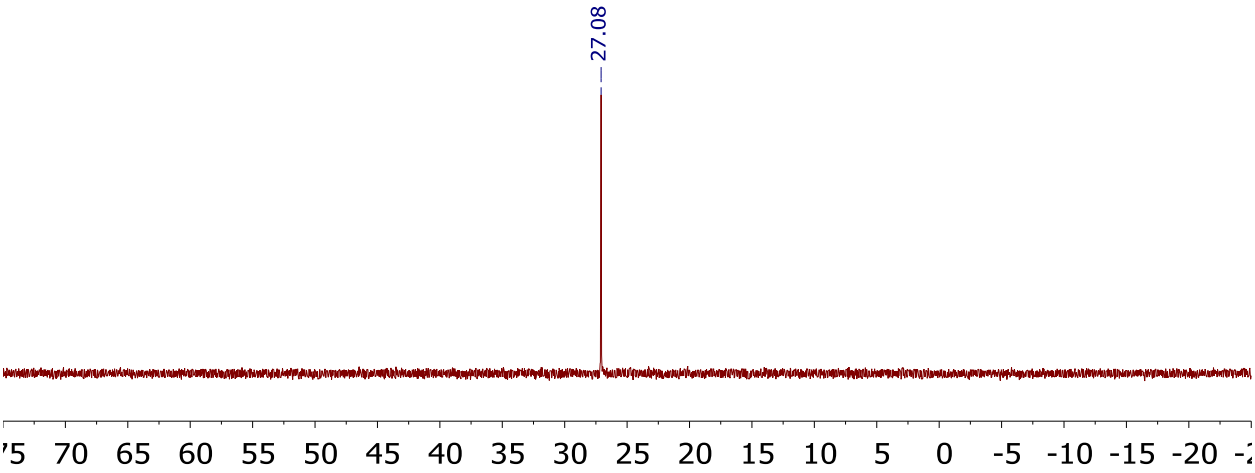


Figure S100. ^{1}H NMR spectrum of **36a** in C_6D_6.

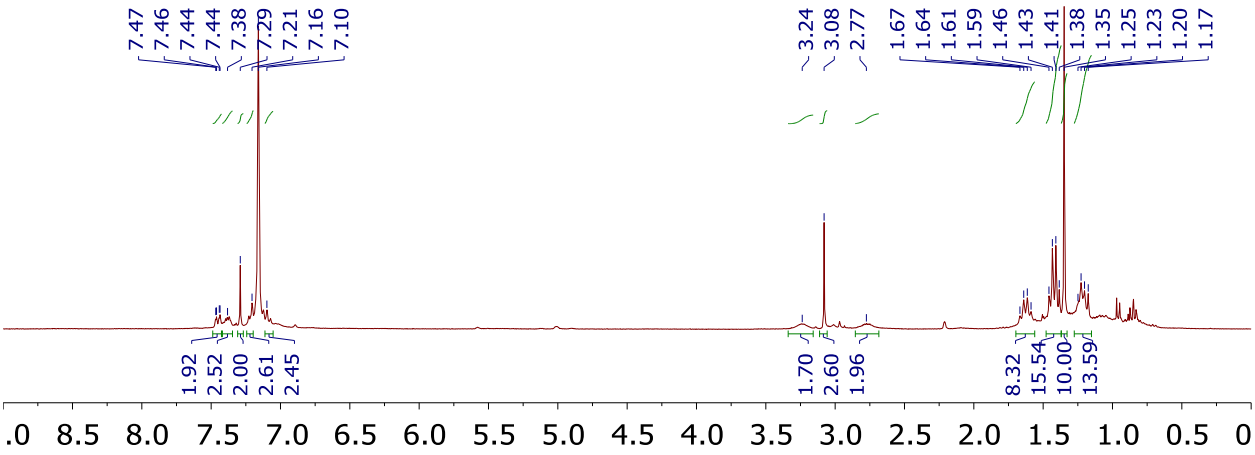


Figure S101. $^{13}C\{^{1}H\}$ NMR spectrum of **36a** in C_6D_6.

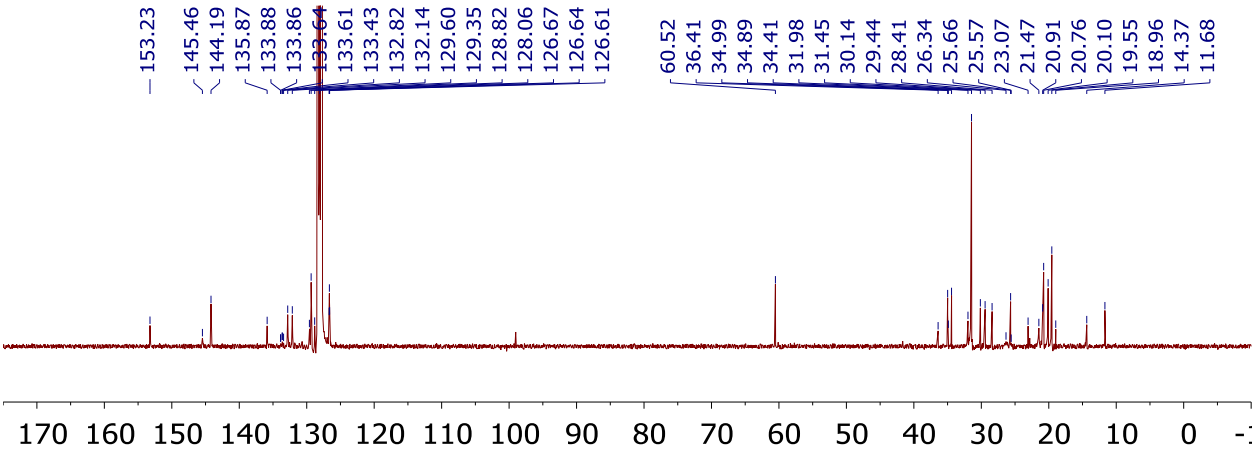


Figure S102. $^{31}P\{^{1}H\}$ NMR spectrum of **36a** in C_6D_6.

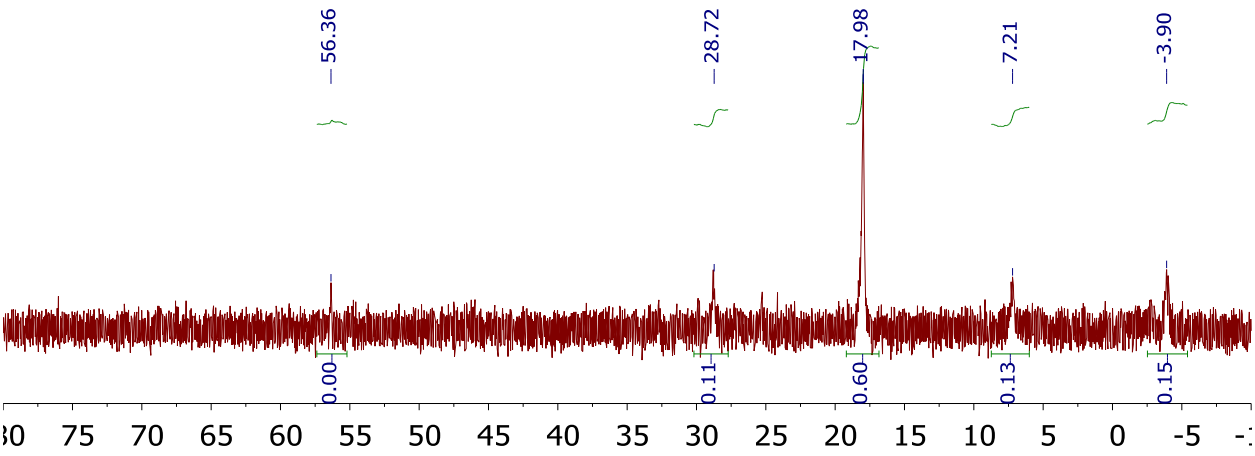


Figure S103. ^{1}H NMR spectrum of **37a** in C_6D_6.

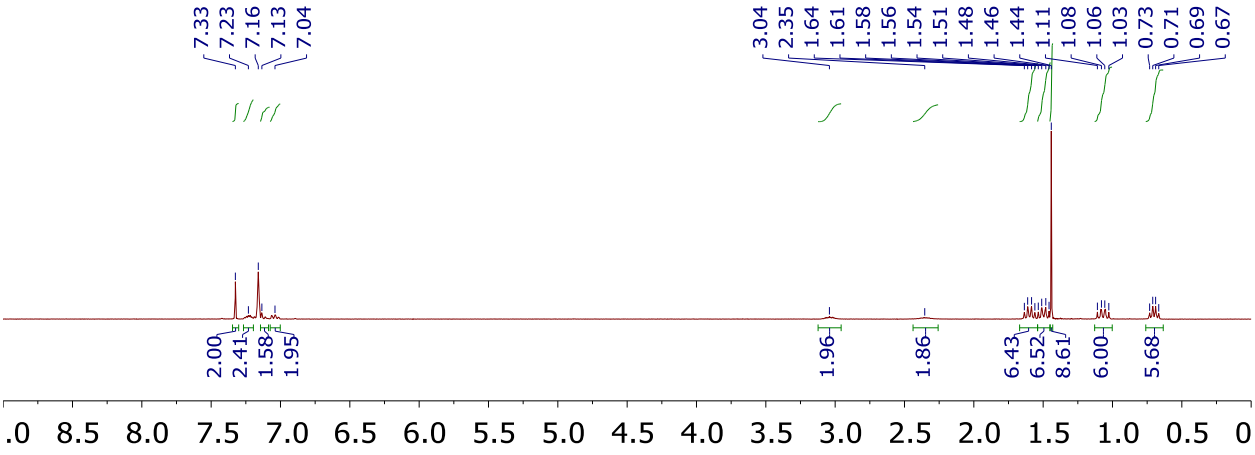


Figure S104. $^{13}C\{^{1}H\}$ NMR spectrum of **37a** in C_6D_6.

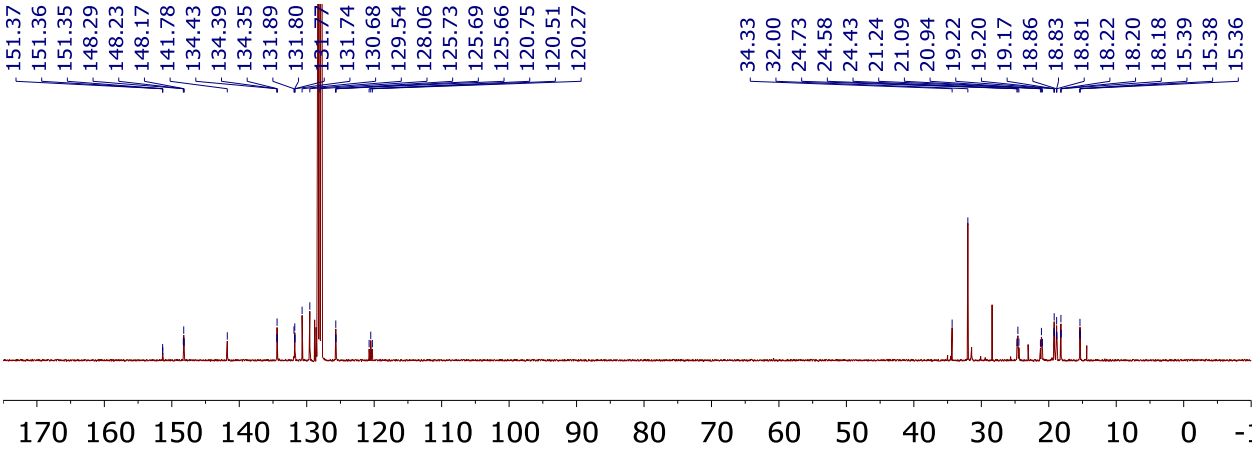


Figure S105. $^{31}P\{^{1}H\}$ NMR spectrum of **37a** in C_6D_6.

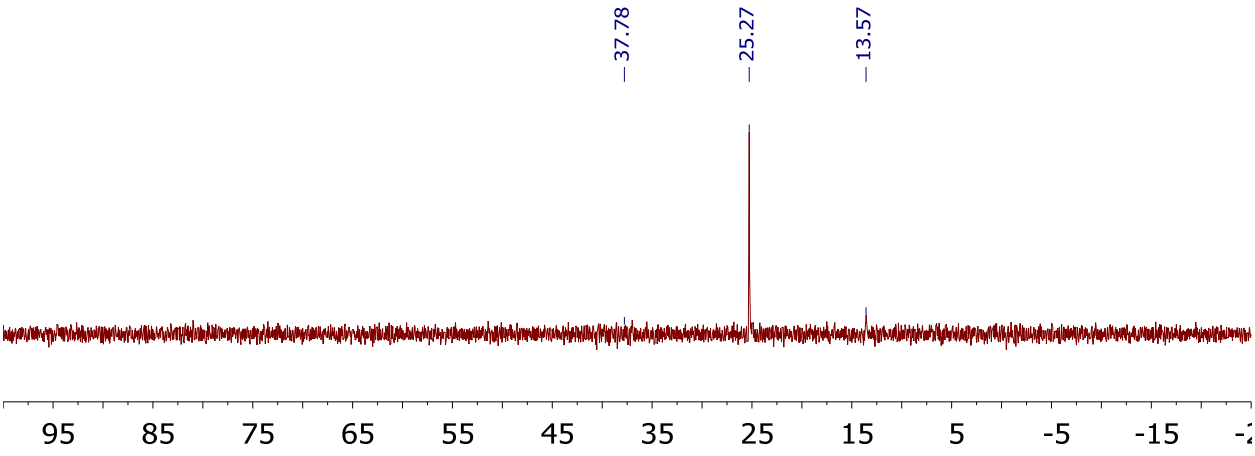


Figure S106. ^{1}H NMR spectrum of **38a** in C_6D_6.